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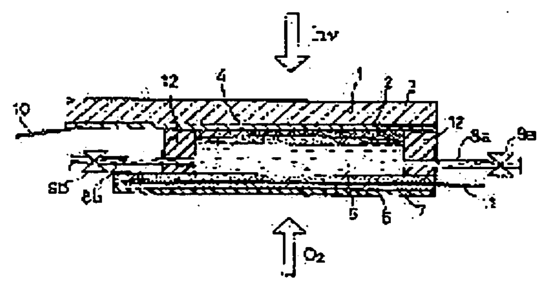
(54) COMPOUND ELECTRODE FOR OXYGEN REDUCTION

(57)Abstract:
PROBLEM TO BE SOLVED: To provide an oxygen reduced compound electrode to which 4-electron reduction reaction is seemingly given at the rate of selection near 100% to electrochemical reduction of oxygen.
SOLUTION: The oxygen reducted compound electrode is constituted so that at least an electrochemical catalyst A, which catalyzes the 2-electrons reduction reaction, which generates hydrogen peroxide by electrochemical reduction of oxygen, and the catalyst B, which catalyzes the decomposition reaction, which decomposes the generated hydrogen peroxide, and generates oxygen, may be contained. By making the electrode potential of the compound electrode for oxygen reduction as the oxygen reduction potential of the electrochemical catalyst A, the electrochemical catalyst A carries out 2-electrons reduction to the oxygen reproduced by decomposing hydrogen peroxide by the catalyst B, then, the hydrogen peroxide is generated repeatedly.



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CLAIMS

[Claim(s)]
[Claim 1] The electrochemistry catalyst A which carries out the catalyst of the 2 electronic reduction reaction which generates a hydrogen peroxide by electrochemistry reduction of oxygen It is the composite electrode for oxygen reduction which contains the catalyst B which carries out the catalyst of the decomposition reaction which disassembles the generated hydrogen peroxide and generates oxygen at least. The electrode potential of the above-mentioned composite electrode is a composite electrode for oxygen reduction which is the oxygen reduction potential of the electrochemistry catalyst A, and the electrochemistry catalyst A returns two electrons of oxygen reproduced by Catalyst B decomposing a hydrogen peroxide, and repeats and generates a hydrogen peroxide.
[Claim 2] The composite electrode for oxygen reduction according to claim 1 which is the metal complex which has the ligand L configurated in the central metal atom alpha by which the above-mentioned electrochemistry catalyst A is expressed with alphaLn (the number of the ligands which n configurates), and this metal atom alpha.
[Claim 3] The composite electrode for oxygen reduction according to claim 2 whose ligand of the above-mentioned metal complex is the single seat which has a nitrogen atom, or a multidentate ligand.
[Claim 4] The composite electrode for oxygen reduction according to claim 3 with which the above-mentioned ligand has a porphyrin ring or a phtalo cyanogen ring.
[Claim 5] The composite electrode for oxygen reduction according to claim 4 with which the above-mentioned Pori Phi Lynne ring or an above-mentioned phtalo cyanogen ring has the substituent of polymerization nature.
[Claim 6] The composite electrode for oxygen reduction of any one publication of five from claim 1 which is the metallic oxide by which the above-mentioned catalyst B is expressed with a hydrogen-peroxide dialytic ferment or betaOx (atomic number of the oxygen beta is decided by the metallic element and it is decided with the valence of a metallic element that x will be).
[Claim 7] The composite electrode for oxygen reduction according to claim 6 whose above-mentioned metallic oxide is a manganic acid ghost expressed with a perovskite oxide or MnOy (atomic number of the oxygen it is decided with the valence of manganese that y will be).
[Claim 8] A metallic material, a carbon material, a metallic oxide, and the metal complex that has the ligand L configurated in the central metal atom alpha expressed with alphaLn (the number of the ligands which n configurates), and this metal atom alpha, since -- with the electrochemistry catalyst A which carries out the catalyst of the 2 electronic reduction reaction which is one sort chosen from the group which changes, and generates a hydrogen peroxide by the electrochemical reduction of oxygen It consists of the metallic oxide expressed with a hydrogen-peroxide dialytic ferment or betaOx (atomic number of the oxygen beta is decided by the metallic element and it is decided with the valence of a metallic element that x will be). The composite electrode for oxygen reduction which includes at least the catalyst B which carries out the catalyst of the decomposition reaction which disassembles the hydrogen peroxide generated according to the electrochemistry catalyst A, and generates oxygen.
[Claim 9] The composite electrode for oxygen reduction according to claim 8 with which the above-mentioned electrochemistry catalyst A and Catalyst B are held at a conductive base material, and change.
[Claim 10] The composite electrode for oxygen reduction according to claim 9 with which the above-mentioned electrochemistry catalyst A serves as a conductive base material.
[Claim 11] The composite electrode for oxygen reduction according to claim 9 or 10 which insulates Catalyst B electrically and changes so that an electron may not move through direct or an electronic conductor between the above-mentioned catalyst B, a conductive base material, and/or the electrochemistry catalysts A.
[Claim 12] The oxygen reduction composite electrode according to claim 11 with which the polymer of proton conductivity distributes and the above-mentioned catalyst B changes.
[Claim 13] The composite electrode for oxygen reduction of any one publication of 12 from claim 8 whose ligand of the above-mentioned metal complex is the single seat which has a nitrogen atom, or a multidentate ligand.
[Claim 14] The composite electrode for oxygen reduction according to claim 13 with which the above-mentioned ligand has a porphyrin ring or a phthalocyanine ring.
[Claim 15] The composite electrode for oxygen reduction according to claim 14 with which the above-mentioned Pori Phi Lynne ring or an above-mentioned phtalo cyanogen ring has the substituent of polymerization nature.
[Claim 16] The composite electrode for oxygen reduction of any one publication of 15 from claim 8 whose above-mentioned metallic oxide is a manganic acid ghost expressed with a perovskite oxide or MnOy (atomic number of the oxygen it is decided with the valence of manganese that y will be).
[Claim 17] The composite electrode for oxygen reduction according to claim 16 whose above-mentioned perovskite oxide is LaxSr1-xMnO3 (x=0-0.5).
[Claim 18] The electrochemistry catalyst A which carries out the catalyst of the 2 electronic reduction reaction which generates a hydrogen peroxide by electrochemistry reduction of oxygen The catalyst B which carries out the catalyst of the decomposition reaction which disassembles the generated hydrogen peroxide and generates oxygen Even if few, it consists of the composite electrode for oxygen reduction to contain, and the electrode potential of the above-mentioned composite electrode is the oxygen reduction potential of the electrochemistry catalyst A. The generation-of-electrical-energy cel which has the positive electrode which the electrochemistry catalyst A returns two electrons of oxygen reproduced by Catalyst B decomposing a hydrogen peroxide, and repeats and generates a hydrogen peroxide, the negative electrode which carries out oxidation reaction of a negative-electrode active material or the fuel matter, and an electrolyte.
[Claim 19] The generation-of-electrical-energy cel according to claim 18 which consists of the metal complex which has the ligand L configurated in the central metal atom alpha by which the above-mentioned electrochemistry catalyst A is expressed with alphaLn (the

number of the ligands which n configurates), and this metal atom alpha, and consists of the metallic oxide by which the above-mentioned catalyst B is expressed with a hydrogen-peroxide dialytic ferment or betaOx (atomic number of the oxygen beta is decided by the metallic element and it is decided with the valence of a metallic element that x will be).
[Claim 20] The generation-of-electrical-energy cel according to claim 18 or 19 which the molecule which is excited by either [at least] the above-mentioned negative electrode or the electrolyte by light absorption, and oxidizes a carbohydrate electrochemically is given [cel], and a carbohydrate is supplied [cel] to this molecule with Mitsuteru putting, makes a carbohydrate oxidize with this molecule in a negative electrode, and generates electromotive force between a positive electrode and a negative electrode.
[Claim 21] The generation-of-electrical-energy cel according to claim 18 or 19 which the above-mentioned generation-of-electrical-energy cel is a fuel cell, the above-mentioned positive electrode and a negative electrode are used as an air pole and a fuel electrode, respectively, and an air pole and a fuel electrode are connected through the ion exchange membrane of proton conductivity, and changes.
[Claim 22] The generation-of-electrical-energy cel according to claim 18 or 19 using the gap or one sort of metals which the above-mentioned generation-of-electrical-energy cel is an air cell, and be chosen as the above-mentioned negative electrode from zinc, magnesium, and aluminum.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the oxygen reduction composite electrode which uses oxygen as the electrode reaction matter. Especially the oxygen reduction composite electrode of this invention is used for an oxygen pole or an air pole of electrochemistry devices, such as fuel cells, such as air cells, such as a zinc-air cell which uses the reduction reaction of oxygen as a positive-electrode reaction, an aluminum-air cell, and a sugar-air cell, and an oxygen hydrogen fuel cell, a methanol fuel cell, etc.
[0002]
[Description of the Prior Art] If electrolytic reduction of the oxygen (O2) is carried out conventionally, at 1 electronic reduction, it is known for generation and 2 electronic reduction of superoxide by generation of a hydrogen peroxide, and 4 electronic reduction that water will generate (JACEK KIPKOWSKI, PHILIP N.ROSS edit, ELECTROCATALYSIS, and WILEY-VCH publication, 1998, 204 - 205 pages). It is required to be large capacity, using the reduction reaction of oxygen as a positive-electrode reaction of a cell, to be the most **** possible potential (plus) about the electrochemistry reduction reaction of the oxygen accompanied by as many electronic transitions as possible, to make an overvoltage as small as possible and to advance it moreover, in order to obtain electrochemistry devices, such as a cell of the high current in the high voltage moreover.
[0003] That is, the catalyst which can moreover cause 4 electronic reduction reaction for an overvoltage small with high potential is desirable. In order to acquire such a catalyst, the measure of former some is reported. The catalyst which becomes JP,2-30141,B and JP,2-30142,B from the conductive powder which supported the metal chelate compound which has oxygen gas reduction ability, such as an iron phthalocyanine and a cobalt porphyrin, and the porosity Plastic solid of a fluororesin is proposed. If the dimer (2 nucleus complex) of metal chelate compound is used, it is said that higher oxygen reduction ability (4 electronic reduction ability) can be expected, and the air cell of a big output can be expected.
[0004] The technique of the oxygen reduction catalyst using large annular complexes which use transition metals, such as Cr, Mn, Fe, and Co, as a central metal, such as a cobalt porphyrin 2 nucleus complex, is the above-mentioned ELECTROCATALYSIS and WILEY-VCH. It is stated to 232 - 234 pages in publication and 1998. The 2 nucleus manganese complex compound catalyst for oxygen reduction is proposed by JP,11-253811,A. This 2 nucleus complex carries out the catalyst of the 4 electronic reduction reaction of oxygen with high selectivity. It is said that a manganese atom takes the valence of 7 ** from divalent, and carries out the catalyst of the oxygen reduction reaction in [potential] minus 0.5V to plus 2V.
[0005]
[Problem(s) to be Solved by the Invention] However, it is not known for what kind of conditions about what kind of catalyst is effective in 1 electronic reduction reaction of oxygen, 2 electronic reduction reaction, and 4 electronic reduction reaction. If the selectivity of 4 electronic reduction reaction changes with complex kinds and what kind of metal complex is used, it is difficult to get to know the technical contents needed [whether it is stabilized and obtained and] for the selectivity to higher 4 electronic reduction reaction in actual use. If it is going to obtain high potential according to the technique indicated until now, a dinuclear metal complex with a central metal atom with a big valence is required. Furthermore, such a dinuclear metal complex It has strong oxidizing power and there is a difficulty of bringing about oxidation degradation, such as other components of the cell used together with such a dinuclear metal complex, for example, the electrolytic solution, an electrode lead, a charge collector, a cell case, a separator, and gas permselective membrane, in actual use.
[0006] This invention solves such a problem, and it offers the oxygen reduction composite electrode which was excellent also in the stability which gives 4 electronic reduction reaction with the selectivity near 100% seemingly to electrochemistry reduction of oxygen, without using the strong catalyst component of oxidizing power, such as a dinuclear metal complex with a central metal with a big valence.
[0007]
[Means for Solving the Problem] In order to solve an above-mentioned technical problem the composite electrode for oxygen reduction of this invention The electrochemistry catalyst A which carries out the catalyst of the 2 electronic reduction reaction which generates a hydrogen peroxide by electrochemistry reduction of oxygen It is the composite electrode for oxygen reduction which contains the catalyst B which carries out the catalyst of the decomposition reaction which disassembles the generated hydrogen peroxide and generates oxygen at least. The electrode potential of the above-mentioned composite electrode is the oxygen reduction potential of the electrochemistry catalyst A, and it is characterized by for the electrochemistry catalyst A returning two electrons of oxygen reproduced by Catalyst B decomposing a hydrogen peroxide, and repeating and generating a hydrogen peroxide.
[0008] The electrochemistry catalyst which performs 2 electronic reduction reaction of the oxygen which the composite electrode for oxygen reduction of this invention returns [oxygen] oxygen 1 molecule at least, and makes hydrogen-peroxide 1 molecule generate, By having the catalyst which performs the decomposition reaction of the hydrogen peroxide which hydrogen-peroxide 1 generated molecule is disassembled [hydrogen peroxide] and reproduces the 1/dyad of oxygen, repeating the above-mentioned 2 electronic reduction reaction and the above-mentioned decomposition reaction, and performing them Seemingly, 4 electronic reduction of oxygen can be performed and 4 electronic reduction reaction of oxygen can be performed in general with 100% of selectivity. Here, it says that the current according that the selectivity of 4 electronic reduction reaction of oxygen is 100% in general to reduction reactions other than 4 electronic reduction reaction of oxygen is not observed substantially.
[0009] It is desirable that it is the metal complex which has the ligand L configurated in the central metal atom alpha expressed with alphaLn (the number of the ligands which n configurates), and this metal atom alpha, and, as for the above-mentioned electrochemistry catalyst A, it is [the above-mentioned catalyst B] desirable that it is the metallic oxide or hydrogen-peroxide dialytic ferment expressed with betaOx (atomic number of the oxygen beta is decided by the metallic element and it is decided with the

valence of a metallic element that x will be). Here, especially the metal complex used for the invention in this application points out the metal complex of a single nucleus, unless it refuses. Since oxidizing power is weak compared with the dinuclear metal complex indicated by the advanced technology, a single nucleus metal complex becomes possible [controlling the oxidation degradation of other components of a cell].

[0010] Moreover, it is desirable that the ligand of a metal complex is the single seat which has a nitrogen atom, or a multidentate ligand. A ligand is a porphyrin ring or a phtalo cyanogen ring still more preferably. Moreover, it is desirable that the Pori Phi Lynne ring or a phtalo cyanogen ring has the substituent of polymerization nature.

[0011] Moreover, the manganic acid ghost expressed with a perovskite oxide or MnOy (atomic number of the oxygen it is decided with the valence of manganese that y will be) can be used for a metallic oxide.

[0012] The electrode for oxygen reduction of this invention can be constituted so that the catalyst B of the following which carries out the catalyst of the decomposition reaction which disassembles the hydrogen peroxide generated at 2 electronic reduction reaction by the following electrochemistry catalysts A and the electrochemistry catalyst A which carry out the catalyst of the 2 electronic reduction reaction which generates a hydrogen peroxide by electrochemistry reduction of oxygen, and generates oxygen may be contained at least.

[0013] Moreover, it is desirable that the electrochemistry catalyst A and Catalyst B are held at the conductive base material, and the electrochemistry catalyst A can also serve as a conductive base material further.

[0014] Moreover, it is desirable to insulate Catalyst B electrically so that an electron may not move through direct or an electronic conductor between Catalyst B, a conductive base material, and/or the electrochemistry catalysts A. Preferably, it is that Catalyst B is distributed by the polymer of proton conductivity.

[0015] One sort chosen from the group which consists of a metallic material, a carbon material, a metallic oxide, and the metal complex that has the ligand L configurated in the central metal atom alpha expressed with alphaLn (the number of the ligands which n configurates), and this metal atom alpha can be used for the electrochemistry catalyst A.

[0016] Moreover, the single seat or multidentate ligand which has a nitrogen atom can be used for the ligand of a metal complex. Preferably, a ligand is having a porphyrin ring or a phthalocyanine ring. Moreover, the Pori Phi Lynne ring or a phtalo cyanogen ring can also have the substituent of polymerization nature.

[0017] The metallic oxide expressed with a hydrogen-peroxide dialytic ferment or betaOx (atomic number of the oxygen beta is decided by the metallic element and it is decided with the valence of a metallic element that x will be) can be used for Catalyst B.

[0018] Moreover, the manganic acid ghost expressed with a perovskite oxide or MnOy (atomic number of the oxygen it is decided with the valence of manganese that y will be) can be used for a metallic oxide. Furthermore, LaxSr1-xMnO3 (x=0-0.5) can be used for a perovskite oxide.

[0019] It is desirable that it is the metal complex which has the ligand L configurated in the central metal atom alpha by which the electrochemistry catalyst A is especially expressed with alphaLn (the number of the ligands which n configurates), and this metal atom alpha, and is the metallic oxide by which Catalyst B is expressed with a hydrogen-peroxide dialytic ferment or betaOx (atomic number of the oxygen beta is decided by the metallic element and it is decided with the valence of a metallic element that x will be).

[0020] A generation-of-electrical-energy cel can be constituted by using the composite electrode for oxygen reduction of this invention as the positive electrode of an air cell which considers the reduction reaction of oxygen as a positive-electrode reaction, or a positive electrode of a fuel cell. Namely, the electrochemistry catalyst A which carries out the catalyst of the 2 electronic reduction reaction whose this invention generates a hydrogen peroxide by electrochemistry reduction of oxygen The catalyst B which carries out the catalyst of the decomposition reaction which disassembles the generated hydrogen peroxide and generates oxygen Even if few, it consists of the composite electrode for oxygen reduction to contain, and the electrode potential of the above-mentioned composite electrode is the oxygen reduction potential of the electrochemistry catalyst A. The electrochemistry catalyst A returns two electrons of oxygen reproduced by Catalyst B decomposing a hydrogen peroxide, and the generation-of-electrical-energy cel which has the positive electrode which repeats and generates a hydrogen peroxide, the negative electrode which carries out oxidation reaction of a negative-electrode active material or the fuel matter, and an electrolyte is offered.

[0021] The above-mentioned generation-of-electrical-energy cel can give the molecule which is excited by either [at least] a negative electrode or the electrolyte by light absorption, and oxidizes a carbohydrate electrochemically, can supply a carbohydrate to this molecule with Mitsuteru putting, makes a carbohydrate able to oxidize with this molecule in a negative electrode, and can be used as the generation-of-electrical-energy cel which generates electromotive force between a positive electrode and a negative electrode and which uses a carbohydrate as a fuel.

[0022] Moreover, in the above-mentioned generation-of-electrical-energy cel, the composite electrode for oxygen reduction of this invention can be made into an air pole, a negative electrode can be used as a fuel electrode, and when an air pole and a fuel electrode make it connect through the ion exchange membrane of proton conductivity, a fuel cell can be constituted.

[0023] Moreover, in the above-mentioned generation-of-electrical-energy cel, a zinc air battery, a magnesium-air cell, and an aluminum-air cell can be constituted by using the composite electrode for oxygen reduction of this invention as a positive electrode, and using the gap or one sort of metals which be chosen as a negative electrode from zinc, magnesium, and aluminum.

[0024]

[Embodiment of the Invention] This invention offers the oxygen reduction composite electrode which uses oxygen as the electrode reaction matter. The composite electrode for oxygen reduction of this invention contains the catalyst B which disassembles the electrochemistry catalyst A which generates a hydrogen peroxide by the electrochemical reduction of oxygen, and the generated hydrogen peroxide, and generates oxygen at least. The electrochemistry catalyst A is O2+H2O+2e-. -> The catalyst of the 2 electronic reduction reaction (1) of the oxygen expressed with OH-+HO2- (inside of lye) is carried out, and a hydrogen peroxide (H2O2, hydrogen-peroxide ion expressed with HO2- in lye) is generated.

[0025] Catalyst B is the generated hydrogen-peroxide ion 2HO2- -> O2 + 2OH- The catalyst of the decomposition reaction (2) expressed is carried out, and oxygen is reproduced. Again, the reproduced oxygen receives 2 electronic reduction according to the electrochemistry catalyst A, and generates hydrogen-peroxide ion. Oxygen 1 molecule generates hydrogen-peroxide ion 1 molecule by 2 electronic reduction reaction (1), and hydrogen-peroxide ion 1 generated molecule reproduces 1-/dyad oxygen by the decomposition reaction (2). A 1-/dyad oxygen molecule generates 1-/dyad hydrogen-peroxide ion by 2 electronic reduction reaction (1), and 1 generated/dyad peroxidation ion reproduces the oxygen of 1/4 molecule by the decomposition reaction (2).

[0026] The oxygen molecule of 1/4 molecule generates the hydrogen-peroxide ion of 1/4 molecule by 2 electronic reduction reaction (1), and the peroxidation ion of 1/4 generated molecule reproduces the oxygen of 1/8 molecule by the decomposition reaction (2). 2 electronic reduction reaction (1) and a decomposition reaction continue occurring (2) Repeatedly. As opposed to reduction of oxygen 1 molecule Namely, two electrons, one electron, 1/2 electron, 1/4 electron, 1/8 electron, ..., n (1/2) Although a total of four electronic (n -> infinity) electrons are used, and it becomes as the same as oxygen 1 molecule underwent 4 electronic reduction reaction with the

potential of 2 electronic reduction reaction, namely, it is 2 electronic reactions The same result is brought as the reaction which is equivalent to 4 twice as many electronic reactions ($O_2+2H_2O+4e^- \rightarrow 4OH^-$) as 2 electronic reactions as quantity of electricity occurred.

[0027] Since the oxygen reduction composite electrode of this invention contains at least the electrochemistry catalyst A and Catalyst B which give the reduction path of such oxygen, it can perform 4 electronic reduction of oxygen with the selectivity near 100%.

[0028] Hereafter, this invention is explained in detail. If oxygen is returned electrochemically and a hydrogen peroxide (H_2O_2 and HO_2^-) is generated as an electrochemistry catalyst A of this invention, organic, inorganic, metals, such mixture, a composite, and any ingredient can be used. Platinum, cobalt, a ruthenium, palladium, nickel, gold, silver, copper, Carbon materials, such as metallic materials, such as a platinum-cobalt alloy and a platinum-ruthenium alloy, a graphite, and activated carbon, Oxidization copper, nickel oxide, cobalt oxide, ruthenium oxide, a lead oxide, molybdenum oxide, Metallic oxides, such as a manganese-dioxide, lead ruthenate, and lanthanum-manganese-copper perovskite oxide, An iron phthalocyanine, a cobalt phthalocyanine, a copper phthalocyanine, a manganese phthalocyanine, Metal complexes, such as the metal phthalocyanine or metalloporphyrin which has porphyrin rings, such as a zinc phthalocyanine, a ruthenium ammine complex, a cobalt ammine complex, and a cobalt ethylenediamine complex, etc. can be used.

[0029] The metal complex made to express with alphaLn with high activity to the electrochemical reduction of oxygen especially is used suitably. When a metal complex is used, there is an advantage that it is changeable in a **** (plus) direction or the **** (minus) direction by it not only changing the class or valence of the main metallic element alpha for the reduction potential of oxygen, but changing Ligand L. For example, alpha can change 50mV of 2 electronic reduction potential of oxygen in the **** (plus) direction from 10 by introducing the carboxyl group (-COOH) of electronic suction nature, a cyano group (-CN), etc. into the phthalocyanine ring which is a ligand with the cobalt phthalocyanine complex (it expresses PcCo (II)) which is divalent cobalt.

[0030] Moreover, the zinc phthalocyanine complex (it expresses PcZn (II)) whose alpha besides PcCo (II) is divalent zinc, and alpha can change 200mV of 2 electronic reduction potential of oxygen in the **** (minus) direction from 10 by introducing electron-donative alkoxy groups, such as an octabutoxy radical (OBu), into a phthalocyanine ring with the copper-phthalocyanine complex (it expresses PcCu (II)) which is divalent copper. Furthermore, with the metal complex which consists of ligands which have proton dissociation-equilibrium ability, 2 electronic reduction potential of oxygen can be changed a lot among several 100mV by changing pH of media, such as the electrolytic solution used in case an oxygen reduction reaction is performed.

[0031] As a ligand (L), a phthalocyanine, an octabutoxy phthalocyanine, OKUTA cyano phthalocyanine and phthalocyanine 4 acetic acid, a tetrapod (O-aminophenyl) porphyrin, A tetra-amino phthalocyanine, a tetramethyl phenyl porphyrin, The ligand which has porphyrin rings, such as tetra-phenyl poly FIRIN and tetrapod (N-methoxyphenyl) Pori Phi Lynne, Ammonia, ethylenediamine, ethylenediaminetetraacetic acid, 4-vinylpyridine, Since the single seat or multidentate ligand which 2-vinylpyridine, a bipyridyl, etc. contain a nitrogen atom (N), and forms a complex with the central metal alpha through this nitrogen atom forms a comparatively stable metal complex, it is desirable. Since ligands, such as a tetra-amino phthalocyanine, tetrapod (O-aminophenyl) Pori Phi Lynne, etc. who have the substituent of polymerization nature, such as an amino group and an aminophenyl radical, especially, can form the metal complex whose stability increased to the pan macromolecule-ized by the polymerization, they are desirable.

[0032] Next, as a main metallic element (alpha) of such a metal complex (alphaLn), since platinum, a ruthenium, cobalt, manganese, iron, copper, silver, zinc, etc. can run the reduction reaction of oxygen with a smaller overvoltage, they are desirable. Moreover, as for the valence of alpha, four or less are desirable. By making a valence or less into four, the oxidizing power of a catalyst can be stopped and oxidation degradation, such as an electrode lead, the cell used together with a metal complex, and other components, for example, the electrolytic solution, a charge collector, a cell case, a separator, and gas permselective membrane, can be prevented effectively.

[0033] Organic [which disassembles a hydrogen peroxide and generates oxygen as a catalyst B of this invention], inorganic, metals, such mixture, a composite, and any ingredient can be used. Moreover, hydrogen-peroxide dialytic ferments, such as a catalase, etc. can be used effectively. Especially, a hydrogen peroxide and compatibility are high and the metallic oxide expressed with high betaOx of the oxygen exchange capacity which incorporates or emits oxygen is desirable. As such a metallic oxide, chemistry oxidation of the divalent manganese salt, such as $MnSO_4$, is carried out with a hydrogen peroxide etc. Manganic acid ghosts, such as Mn_2O_3 obtained by carrying out heating oxidation in the ambient atmosphere which contains oxygen gas further if needed, Mn_3O_4, Mn_5O_8, and gamma-MnOOH (Mn_3O_4 and mixture of Mn_5O_8) (MnO_y), platinum black, ruthenium oxide, $Cu_{x-1}Sr_xTiO_3$ (x=0-0.5), and $La_xSr_{1-x}MnO_3$ (x=0-0.5) and $SrTiO_3$ etc. -- there is a perovskite oxide etc. Especially, the decomposition activity of a hydrogen peroxide is high, and there is little degradation, and since the manganese low-grade oxide is moreover cheap, it is desirable. A manganese low-grade oxide is a manganic acid ghost with which the valence of a manganese atom does not fill 4, and since remaining as it is or the calcinated thing can be used for the manganese-dioxide positive electrode of the manganese dry battery after use, it is desirable also especially from a viewpoint of resource reuse.

[0034] The composite electrode for oxygen reduction of this invention has the conductive base material holding the electrochemistry catalyst A and Catalyst B. A conductive base material can consist of a metallic material, a carbonaceous ingredient, a conductive oxide ingredient, etc., and the thing of various configurations, such as tabular, a cylinder, cylindrical, the shape of a disk, and a porous body, can be used for it, and it can also serve as a charge collector.

[0035] In addition, the electrochemistry catalyst A can also serve as a conductive base material. In this case, it is necessary to make Catalyst B hold on the front face of the electrochemistry catalyst A.

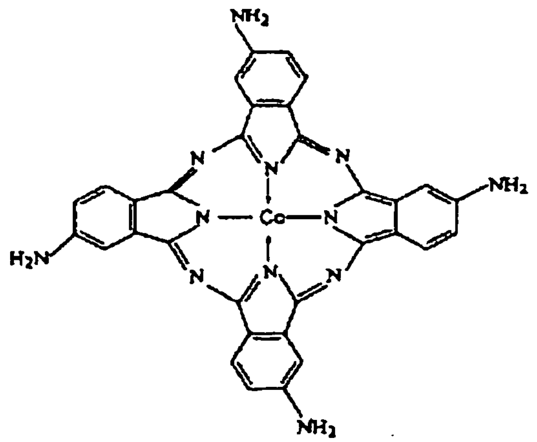
[0036] Although it is in the composite electrode for oxygen reduction of this invention, and the electrochemistry catalyst A and Catalyst B may be arranged in contact with each other or you may separate and arrange, arranging near the partner to each other is desirable. Not through a migration process, it can result and decompose into Catalyst B through migration of the minimum distance, the hydrogen peroxide generated by the electrochemical reduction of oxygen in the electrochemistry catalyst A by carrying out like this can reproduce oxygen, and the reproduced oxygen can receive reduction in the electrochemistry catalyst A very much through migration of the minimum distance not through a migration process too. The overvoltage of oxygen reduction can be made small as the whole composite electrode for oxygen reduction. Furthermore, if a metal complex is used as an electrochemistry catalyst A, since, as for the metal complex, molecule each has oxidation reduction capacity, the electrochemistry catalyst A and Catalyst B can be approached to molecule order, and the composite electrode for oxygen reduction of a smaller overvoltage is obtained.

[0037] in order to receive supply from the electrode which performs the electrochemical oxidation reaction which uses an electron required for the electrochemical reduction of oxygen combining the composite electrode for oxygen reduction, the electrochemistry catalyst A is held on a conductive base material -- having -- an electrode lead and/or connection -- it connects with a conductor electrically.

[0038] On the other hand, the need of being held on the conductive base material does not not necessarily have Catalyst B. It is desirable to be arranged in the condition of having insulated from these electrically rather. It becomes possible to also use the ingredient which has both operations which performs operation which disassembles a hydrogen peroxide and generates oxygen by

arranging Catalyst B in the condition of having insulated electrically, and electrolytic reduction of oxygen as a catalyst B. In this case, since it is arranged in the condition of having insulated electrically, electrochemical reaction does not occur, but Catalyst B can cause only disassembly of the hydrogen peroxide which generates oxygen.
[0039] Therefore, the electrode potential of the composite electrode for oxygen reduction of this invention is determined by only the oxygen reduction potential of the electrochemistry catalyst A, and it becomes easy to design [of the electrochemistry device using said electrode] it. Moreover, even if it is an ingredient [activity / decomposition reaction / the reduction reaction of oxygen besides the ingredient shown previously, and / both / of a hydrogen peroxide / as a catalyst B], it can use. As such an ingredient, there are platinum, gold, a ruthenium, palladium, a manganese dioxide, activated carbon, a graphite, a metalloporphyrin compound, and a metal phthalocyanine compound. Furthermore, it can prevent effectively that the generated hydrogen peroxide reacts with the returned kind generated by excessive electrochemical reaction, and is consumed since excessive electrochemical reaction except the reduction reaction of oxygen does not occur, or the reproduced oxygen reacts with the oxidized kind generated by excessive electrochemical reaction, and is consumed, and 4 electronic reduction reaction of oxygen is attained with the selectivity seemingly near 100% in it.
[0040] If it is the electrochemistry catalyst A which returns oxygen and generates a hydrogen peroxide, there will be no limit in compound-izing which catalyst B which disassembles a hydrogen peroxide and generates oxygen, and using it. However, in case generation-of-electrical-energy cels, such as an air cell and a fuel cell, are constituted combining the negative electrode which supplies an electron to a positive electrode through an external circuit, using the composite electrode for oxygen reduction of this invention as a positive electrode, when there is a possibility the electrode active material or the fuel matter used for a negative electrode may dissolve in an electrolyte, and may contact a positive electrode, the combination of the high electrochemistry catalyst A of the selectivity of an oxygen reduction reaction and the high catalyst B of the selectivity of disassembly of a hydrogen peroxide can choose suitably. With the fuel cell used as a fuel, saccharides, such as a methanol which dissolves in an electrolyte, ethanol, ethylene glycol, and a glucose The high metal phthalocyanine complex of the selectivity of an oxygen reduction reaction and a metal Pori Phi Lynne complex are chosen as the electrochemistry catalyst A. As a catalyst B It is desirable to choose and compound-ize enzymes, such as a catalase in which oxidizing power has high selectivity to disassembly of manganese low-grade oxides, such as low high Mn 2O3 of peroxidation hydrocracking ability and Mn 5O8, or a hydrogen peroxide, and to use as a composite electrode for oxygen reduction of this invention.

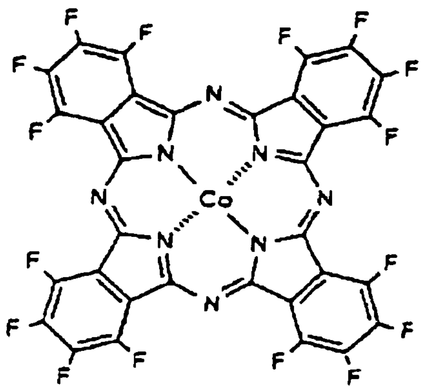
[0041] In order to produce the composite electrode for oxygen reduction of this invention and to make the electrochemistry catalyst A and Catalyst B hold to a conductive base material, dry process, such as the applying method which applies coating liquid including a catalyst, and wet methods, such as the electrochemical depositing method, or vacuum evaporation technique, or the approach of sticking by pressure the catalyst bed made into the shape of a sheet using the binder to a conductive base material can be used. For example, in the case of the applying method, it is desirable to apply coating liquid including the electrochemistry catalyst A to the front face of a conductive base material, to form the 1st catalyst bed, to apply coating liquid including Catalyst B and to form the 2nd catalyst bed on the 1st catalyst bed. It is for Catalyst B to prevent contacting directly to a conductive base material.
[0042] Moreover, it is desirable to make the coating liquid which faces to form the 2nd catalyst bed and includes Catalyst B contain, the polymer, for example, the perfluoro sulfonic-acid polymer, of proton conductivity. Promptly, since the hydroxide ion generated by the decomposition reaction of a hydrogen peroxide by making the 2nd catalyst bed contain the polymer of proton conductivity reacts with a proton and is removed, it becomes possible to promote the decomposition reaction of a hydrogen peroxide of it more.
[0043] Moreover, if electrolytic deposition or electrolytic polymerization is possible for the catalyst itself, it makes it deposit on a conductive base material by approaches, such as constant potential, constant current, or a potential sweep, and can form a catalyst bed. For example, if the metal complex which has ligands which have the substituent of polymerization nature, such as an aforementioned amino group, an aforementioned aminophenyl radical, etc., such as a tetra-amino phthalocyanine and a tetrapod (O-aminophenyl) porphyrin, is used for the electrochemistry catalyst A, the catalyst bed which consists of the metal complex macromolecule-ized through the amino group by electrolytic polymerization can be formed. On the catalyst bed which consists of this macromolecule-ized metal complex, the catalyst bed which includes Catalyst B by the applying method or the electrochemistry depositing method can be formed.
[0044] as the electrolytic solution used combining the composite electrode for oxygen reduction of this invention -- a water solution and the organic electrolytic solution -- any electrolytic solution can be used. especially since the alkaline low-concentration water solution of quick 1M less or equal of a diffusion rate with the large and solubility of O2 can cause an electrolysis reaction efficiently, it is desirable. Hereafter, an example explains this invention concretely.
[0045]
[Example] (Example 1)
(1) a test electrode -- 11 -- 12 -- 13 -- 14 -- 15 -- production -- electrochemistry -- a catalyst -- A -- ****** -- Pori - cobalt - four -- four -- ' -- four -- " -- four -- ' -- " - tetra--- amino -- a phthalocyanine (p-CoTAPc) -- a catalyst -- B -- ****** -- gamma-MnOOH (mixture of Mn 3O4 and Mn5O8) -- using -- glassy carbon (GC) with a diameter of 6mm -- using -- a test electrode -- having produced . Glassy carbon was a pellet with 5mm [in thickness], and a diameter of 6mm, it connected one field with electrode lead wire, and after another field had been exposed, it embedded it in the sheath with a diameter [of 10mm], and a die length of 80mm made of polyimide resin. GC in the condition of forming nothing on the exposed field was used as the test electrode 13.
[0046] 0.1 -- M -- not getting -- an acid -- tetrabutylammonium -- having dissolved -- dimethyl -- a staple fiber -- HOKISHIDO (DMSO) -- a solution -- ** -- one -- having been shown -- a structure expression -- having -- cobalt - four -- four -- ' -- four -- " -- four -- ' -- " - tetra--- amino -- a phthalocyanine (CoTAPc) -- 0.2 -- mM -- the dissolution -- carrying out -- things -- the electrolytic solution -- having created . In this electrolytic solution, it electrolyzed by having used the counter electrode and the Ag/AgCl (saturation KCl) electrode as the reference electrode for platinum by using GC into an operation pole, and p-CoTAPc was formed on the field which GC exposed.
[0047] Electrolysis is repeating the potential of GC 30 times at the rate of 50 mV/s between plus 0.5V and minus 1.4V to an Ag/AgCl reference electrode, and performing increase and decrease for it, and formed p-CoTAPc on GC. This was made into the electrode 12. here -- p-CoTAPc -- CoTAPc -- four -- four -- ' -- four -- " -- four -- " -- ' -- about -- the amino group -- electrolytic oxidation -- winning popularity -- this amino group -- minding -- a macromolecule ---izing .
[0048]
[Formula 1]



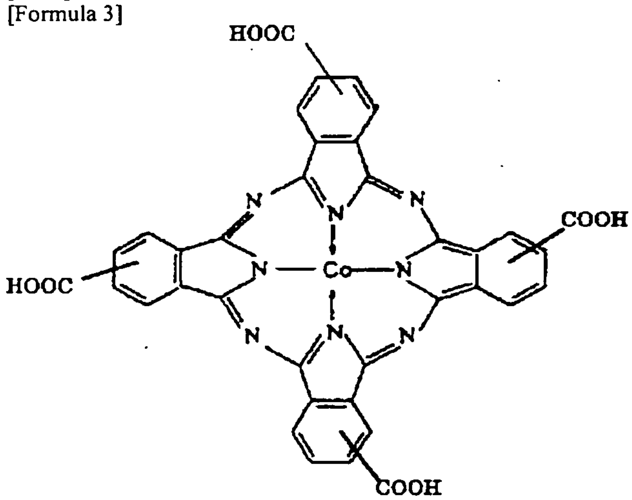
[0049] Next, 25micro of gamma-MnOOH powder was distributed g times in 5micro of ethanol solutions l which dissolved the perfluoro sulfonic-acid polymer (Du Pont make: Nafion112) of proton conductivity 0.05% of the weight, and it was dropped so that the whole surface of GC which formed above-mentioned p-CoTAPc for this might be covered. Next, warm air desiccation of this was carried out, ethanol was evaporated, 5micro of these solutions was dropped further l times, and the test electrode 11 was produced by evaporating ethanol.
[0050] Next, the above-mentioned ethanol solution which distributed gamma-MnOOH was dropped so that the whole surface of GC of 5microl and nakedness might be covered, the loop of the actuation of evaporating ethanol was carried out twice, and the test electrode 14 was produced.
[0051] Next, the above-mentioned ethanol solution which distributed gamma-MnOOH was dropped so that the whole surface of the golden (Au) electrode of 5microl and nakedness might be covered, the loop of the actuation of evaporating ethanol was carried out twice, and the test electrode 15 was produced. It is a pellet with a die length [of 5mm], and a diameter of 6mm, Au electrode used here connects one field with electrode lead wire, where the field of another side is exposed, is embedded into the sheath with a diameter [of 10mm], and a die length of 80mm made from polyimide, and produces it.
[0052] (2) 3 pole cel which uses as a working electrode the test electrode produced according to the process beyond evaluation of the oxygen reduction property of a test electrode, and uses a counter electrode and an Ag/AgCl (saturation KCl) electrode as a reference electrode for platinum was constituted, and the reduction property of oxygen was evaluated. The 0.1M phosphoric acid buffer solution of pH7.4 was used for the electrolytic solution. Electrolysis was performed after dissolved oxygen was saturated [be / it / under / electrolytic-solution / leading] for 30 minutes in oxygen gas. The potential of a working electrode was increased at the rate of 50 mV/s toward 0V, when it decreased at the rate of 50 mV/s from +0.1V to -1.2V to the reference electrode and having been amounted to -1.2V, and the electrolytic current which flows between a working electrode and counter electrodes was recorded to the potential of a working electrode at this time.
[0053] Drawing 1 is the current-potential curve obtained about test electrodes 11, 12, and 13. In drawing 1 , the summit potential (Ep) of the reduction current corresponding to the reduction reaction of oxygen was [at -0.45V and a test electrode 12] -0.75V in the test electrode 11 in -0.35V and a test electrode 13.
[0054] The reduction potential of oxygen is shifted to a plus-in -0.75V to -0.35--0.45V side by forming p-CoTAPc on GC, and oxygen can be returned more by electropositive potential. The test electrode 11 of this invention which compound-ized p-CoTAPc (electrochemistry catalyst A) and MnOOH (catalyst B) acquired the twice [about] as many oxygen reduction peak current value as this compared with the test electrode 12 of only p-CoTAPc. Since the reaction cycle to which the oxygen which the hydrogen peroxide generated by 2 electronic reduction of oxygen decomposed according to an operation of MnOOH, reproduced oxygen, and reproduced according to an operation of p-CoTAPc is returned by p-CoTAPc happens repeatedly and this is equivalent to 4 electronic reduction of oxygen, a twice as many peak current value as this considers it to be a ****** thing. That is, at the test electrode 11 according to this invention, the selectivity near about 100% was able to perform electronic reduction by electropositive potential more.
[0055] drawing 2 showed the current-time curve at the time of performing a controlled potential electrolysis continuously with each summit potential (Ep) about each of test electrodes 11, 12, and 13 -- it comes out. as for a current, any test electrode reaches the stationary current value (Ist) of about 1 law in about 30 seconds after electrolysis initiation. A stationary current value is 25microA in the test electrode 11 which follows 12-13microA and this invention in the test electrodes 12 and 13 of the example of a comparison. In the test electrode 11, compared with a test electrode 12 or 13, a twice [about] as many stationary current value as this is given, and oxygen is seemingly returned with the selectivity near about 100% at 4 electronic reactions.
[0056] Ep value, the Ist value 200 seconds after a controlled potential electrolysis, and the Ist value of 120 hours after were collectively shown in Table 1 about each of test electrodes 11, 12, 13, 14, and 15.
[0057] In addition, the controlled potential electrolysis was performed, blowing oxygen gas into the electrolytic solution.
[0058]
[Table 1]

試験電極	電気化学触媒A	触媒B	酸素還元電流のピーク電位 Ep(V) vs. Ag/AgCl	ピーク電位での定電位電解時の定常電流値 Ist.(μA)	
				電解200秒後	電解120時間後
11	p-CoTAPc	MnOOH	−0.45	25	23
12	p-CoTAPc	…	−0.35	13	12
13	GC	…	−0.75	13	…
14	GC	MnOOH	−0.75	18	…
15	Au	MnOOH	−0.35	24	…
21	CoTAPc	MnOOH	−0.40	26	15
22	CoTAPc	…	−0.35	12	6
31	CoHFPc	MnOOH	−0.20	15	…
32	CoHFPc	…	−0.15	8	…
41	CoCOOHPc	MnOOH	−0.15	20	…
42	CoCOOHPc	…	−0.05	11	…
51	CoOBuPc	MnOOH	−0.35	28	…
52	CoOBuPc	…	−0.25	16	…
61	p-CoTAPc	カタラーゼ	−0.35	29	…
62	CoHFPc	カタラーゼ	−0.15	18	…
63	CoCOOHPc	カタラーゼ	−0.05	22	…
64	CoOBuPc	カタラーゼ	−0.25	30	…
65	GC	カタラーゼ	−0.75	22	…
66	Au	カタラーゼ	−0.35	26	…
71	p-CoTAPc	$La_{0.8}Sr_{0.2}MnO_3$	−0.40	27	…
72	CoHFPc	$La_{0.8}Sr_{0.2}MnO_3$	−0.15	16	…
73	CoCOOHPc	$La_{0.8}Sr_{0.2}MnO_3$	−0.10	20	…
74	CoOBuPc	$La_{0.8}Sr_{0.2}MnO_3$	−0.25	28	…
75	GC	$La_{0.8}Sr_{0.2}MnO_3$	−0.75	21	…
76	Au	$La_{0.8}Sr_{0.2}MnO_3$	−0.35	25	…

[0059] (Example 2)
(3) The test electrode was produced as a production electrochemistry catalyst A of test electrodes 21 and 22 using GC with a same diameter [the / as an example 1] of 6mm, using gamma-MnOOH (mixture of Mn 3O4 and Mn5O8) as a cobalt-tetra-amino phthalocyanine (CoTAPc) and a catalyst B.
[0060] After being dropped so that all the fields where GC exposed 5micro of N and N' solutions l which dissolved in -dimethylformamide (DMF) for CoTAPc of 1mM might be covered, the test electrode 22 which has CoTAPc on a front face by carrying out warm air desiccation for 2 hours was created. Next, warm air desiccation is dropped and carried out, ethanol was evaporated so that the whole surface of GC which has CoTAPc for 5micro of ethanol solutions l which distributed 25micro of gamma-MnOOH powder g times, and dissolved Nafion 0.05% of the weight might be covered, 5micro of these solutions was dropped further l times, ethanol was evaporated, and the test electrode 21 according to this invention which has CoTAPc and MnOOH on a front face was produced.
[0061] (4) 3 pole cel which uses as a working electrode the test electrode produced according to the process beyond evaluation of the oxygen reduction property of a test electrode, and uses a counter electrode and an Ag/AgCl (saturation KCl) electrode as a reference electrode for platinum was constituted, and the reduction property of oxygen was evaluated. The 0.1M phosphoric acid buffer solution of pH7.4 was used for the electrolytic solution. Electrolysis was performed after dissolved oxygen was saturated [be / it / under / electrolytic-solution / leading] for 30 minutes in oxygen gas. The potential of a working electrode was increased at the rate of 50 mV/s toward 0V, when it decreased at the rate of 50 mV/s from +0.1V to -1.2V to the reference electrode and having been amounted to -1.2V, and the electrolytic current which flows between a working electrode and counter electrodes was recorded to the potential of a working electrode at this time.
[0062] The test electrode 21 of this invention which compound-ized CoTAPc (electrochemistry catalyst A) and MnOOH (catalyst B) gave the twice [about] as many oxygen reduction peak current value as this compared with the test electrode 22 of only CoTAPc. The summit potential (Ep) of the reduction current corresponding to the reduction reaction of oxygen was shown in Table 1. In a test electrode 21, it is -0.35V at -0.40V and a test electrode 22. The reduction potential of oxygen is shifted to a plus-in -0.75V to -0.40--0.35V side, and can return oxygen by electropositive potential more.
[0063] Next, the controlled potential electrolysis was continuously performed with each summit potential (Ep) about each of test electrodes 21 and 22. The Ist value after a controlled potential electrolysis is shown in Table 1. Stationary current values are 26microA (after 200 seconds), and 15microA (120 hours after) in the test electrode 21 which follows this invention in the test electrode 22 of the example of a comparison to being 12microA (after 200 seconds), and 6microA (120 hours after). In the test electrode 21, compared with a test electrode 22, a twice [about] as many stationary current value as this is given, and oxygen is returned with the selectivity near about 100% at 4 electronic reactions.
[0064] (Example 3)
(5) The test electrode was produced using GC with a same diameter [the / as an example 1] of 6mm, using gamma-MnOOH (mixture of Mn 3O4 and Mn5O8) as the cobalt-hexa deca fluoro phthalocyanine (CoHFPc) which has the structure expression shown in ** 2 as a production electrochemistry catalyst A of test electrodes 31 and 32, and a catalyst B.
[0065]
[Formula 2]

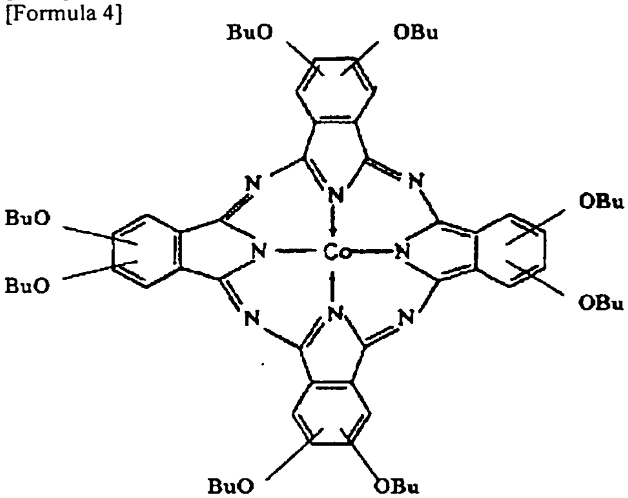


[0066] After being dropped so that all the fields where GC exposed 5micro of 1 DMF solutions l which dissolved CoHFPc of mM in DMF might be covered, warm air desiccation was carried out for 2 hours, the 5micro of the still more nearly same DMF solutions l was dropped, and the test electrode 32 which has CoHFPc on a front face was produced by carrying out warm air desiccation for 2 hours.
[0067] Once it was dropped so that all the fields where GC, on the other hand, exposed 5micro of solutions l which distributed the gamma-MnOOH powder of 50microg in said DMF solution might be covered, warm air desiccation was carried out for 2 hours. Furthermore, the test electrode 31 which follows this invention which uses CoHFPc and MnOOH as a front face by dropping and carrying out warm air desiccation and evaporating DMF so that the whole surface of GC which has CoHFPc for said DMF solution may be covered was produced.
[0068] (6) 3 pole cel which uses as a working electrode the test electrode produced according to the process beyond evaluation of the oxygen reduction property of a test electrode, and uses a counter electrode and an Ag/AgCl (saturation KCl) electrode as a reference electrode for platinum was constituted, and the reduction property of oxygen was evaluated. The 0.1M phosphoric acid buffer solution of pH7.4 was used for the electrolytic solution. Electrolysis was performed after dissolved oxygen was saturated [be / it / under / electrolytic-solution / leading] for 30 minutes in pure oxygen gas. The potential of a working electrode was increased at the rate of 50 mV/s toward 0V, when it decreased at the rate of 50 mV/s from +0.1V to -1.2V to the reference electrode and having been amounted to -1.2V, and the electrolytic current which flows between a working electrode and counter electrodes was recorded to the potential of a working electrode at this time.
[0069] In the test electrode 31 according to this invention which compound-ized CoHFPc (electrochemistry catalyst A) and MnOOH (catalyst B), the twice [about] as many oxygen reduction peak current value as this was given compared with the test electrode 32 of only CoHFPc. The summit potential (Ep) of the reduction current corresponding to the reduction reaction of oxygen is shown in Table 1. In a test electrode 31, it is -0.15V at -0.20V and a test electrode 22. The reduction potential of oxygen is shifted to a plus-in -0.75V to -0.15--0.20V side, and can return oxygen by electropositive potential more.
[0070] Next, the controlled potential electrolysis was continuously performed with each summit potential (Ep) about each of test electrodes 31 and 32. The Ist value 200 seconds after a controlled potential electrolysis is shown in Table 1. A stationary current value is 15microA in the test electrode 31 which follows this invention to being 8microA in the test electrode 22 of the example of a comparison. In the test electrode 31, compared with a test electrode 32, a twice [about] as many stationary current value as this is given, and oxygen is seemingly returned with the selectivity near about 100% at 4 electronic reactions.
[0071] (Example 4)
(7) The test electrode was produced as a production electrochemistry catalyst A of test electrodes 41 and 42 using GC with a same diameter [the / as an example 1] of 6mm to ** 3, using gamma-MnOOH (mixture of Mn 3O4 and Mn5O8) as the cobalt-tetra-carboxy phthalocyanine (CoCOOHPc) which showed the structure expression, and a catalyst B.
[0072]
[Formula 3]



[0073] After being dropped so that all the fields where GC exposed 5micro of 1 DMF solutions l which dissolved CoCOOHPc of mM in DMF might be covered, the test electrode 42 which has CoCOOHPc on a front face was produced by carrying out warm air desiccation for 2 hours, and the 5micro of the still more nearly same DMF solutions l being dropped, and carrying out warm air desiccation for 2 hours.

[0074] The test electrode 41 according to this invention which warm air desiccation is dropped and carried out, and DMF is evaporated, and has CoCOOHPc and MnOOH on a front face so that the whole surface of GC which has CoCOOHPc which, on the other hand, created 5micro of solutions l which distributed the gamma-MnOOH powder of 50microg in said DMF solution by dropping and carrying out warm air desiccation of the 5micro of said DMF solutions l only at once for 2 hours may be covered was produced.
[0075] (8) 3 pole cel which uses as a working electrode the test electrode produced according to the process beyond evaluation of the oxygen reduction property of a test electrode, and uses a counter electrode and an Ag/AgCl (saturation KCl) electrode as a reference electrode for platinum was constituted, and the reduction property of oxygen was evaluated. The 0.1M phosphoric acid buffer solution of pH7.4 was used for the electrolytic solution. Electrolysis was performed after dissolved oxygen was saturated [be / it / under / electrolytic-solution / leading] for 30 minutes in oxygen gas. The potential of a working electrode was increased at the rate of 50 mV/s toward 0V, when it decreased at the rate of 50 mV/s from +0.1V to -1.2V to the reference electrode and having been amounted to -1.2V, and the electrolytic current which flows between a working electrode and counter electrodes was recorded to the potential of a working electrode at this time.
[0076] In the test electrode 41 according to this invention which compound-ized CoCOOHPc (electrochemistry catalyst A) and MnOOH (catalyst B), the twice [about] as many oxygen reduction peak current value as this was given compared with the test electrode 42 of only CoCOOHPc. The summit potential (Ep) of the reduction current corresponding to the reduction reaction of oxygen is shown in Table 1. In a test electrode 41, it is -0.05V at -0.15V and a test electrode 42. The reduction potential of oxygen is shifted to a plus-in -0.75V to -0.05--0.15V side, and can return oxygen by electropositive potential more.
[0077] Next, the controlled potential electrolysis was continuously performed with each summit potential (Ep) about each of test electrodes 41 and 42. The Ist value 200 seconds after a controlled potential electrolysis is shown in Table 1. A stationary current value is 20microA in the test electrode 41 which follows this invention to being 11microA in the test electrode 42 of the example of a comparison. In the test electrode 41, compared with the test electrode 42, the twice [about] as many stationary current value as this was given, and oxygen was seemingly returned with the selectivity near about 100% at 4 electronic reactions.
[0078] (Example 5)
(9) The test electrode was produced as a production electrochemistry catalyst A of test electrodes 51 and 52 using GC with a same diameter [the / as an example 1] of 6mm to ** 4, using gamma-MnOOH (mixture of Mn 3O4 and Mn5O8) as the cobalt-octabutoxy phthalocyanine (CoOBuPc) which showed the structure expression, and a catalyst B.
[0079]
[Formula 4]



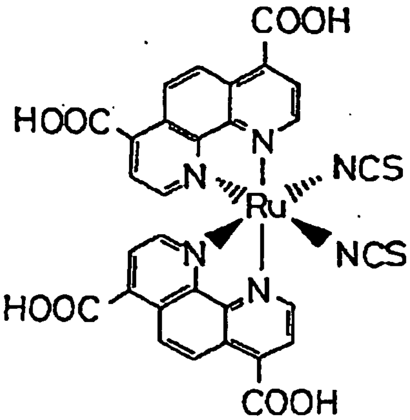
[0080] CoOBuHPc of 1mM was dissolved in DMF which dissolved the Polly 4-vinylpyridine of oxygen permeability 0.05% of the weight. After being dropped so that all the fields where GC exposed 5micro of this DMF solution l might be covered, the test electrode 52 which has CoOBuPc on a front face was created by carrying out warm air desiccation for 2 hours, and the 5micro of the still more nearly same DMF solutions l being dropped, and carrying out warm air desiccation for 2 hours. After being dropped so that all the fields where GC, on the other hand, exposed 5micro of solutions l which distributed 50micro of gamma-MnOOH powder g in said DMF solution might be covered, warm air desiccation was carried out for 2 hours. The test electrode 51 which follows this invention which has CoOBuPc and MnOOH on a front face by dropping and carrying out warm air desiccation and evaporating DMF in the 5micro of the still more nearly same solutions l was produced.
[0081] (10) 3 pole cel which uses as a working electrode the test electrode produced according to the process beyond evaluation of the oxygen reduction property of a test electrode, and uses a counter electrode and an Ag/AgCl (saturation KCl) electrode as a reference electrode for platinum was constituted, and the reduction property of oxygen was evaluated. The 0.1M phosphoric acid buffer solution of pH7.4 was used for the electrolytic solution. Electrolysis was performed after dissolved oxygen was saturated [be / it / under / electrolytic-solution / leading] for 30 minutes in pure oxygen gas. The potential of a working electrode was increased at the rate of 50 mV/s toward 0V, when it decreased at the rate of 50 mV/s from +0.1V to -1.2V to the reference electrode and having been amounted to -1.2V, and the electrolytic current which flows between a working electrode and counter electrodes was recorded to the potential of a working electrode at this time.
[0082] In the test electrode 51 according to this invention which compound-ized CoOBuPc (electrochemistry catalyst A) and MnOOH (catalyst B), the twice [about] as many oxygen reduction peak current value as this was given compared with the test electrode 52 of only CoCOOHPc. The summit potential (Ep) of the reduction current corresponding to the reduction reaction of oxygen is shown in Table 1. In a test electrode 51, it is -0.25V at -0.35V and a test electrode 52. The reduction potential of oxygen is shifted to a plus-in -0.75V to -0.35--0.25V side, and can return oxygen by electropositive potential more.
[0083] Next, the controlled potential electrolysis was continuously performed with each summit potential (Ep) about each of test electrodes 51 and 52. The Ist value 200 seconds after a controlled potential electrolysis is shown in Table 1. A stationary current value is 28microA in the test electrode 51 which follows this invention to being 16microA in the test electrode 52 of the example of a

comparison. In the test electrode 51, compared with the test electrode 52, the twice [about] as many stationary current value as this was given, and oxygen was seemingly returned with the selectivity near about 100% at 4 electronic reactions.
[0084] (Example 6)
(11) The test electrode was produced using GC with a same diameter [the / as an example 1] of 6mm using p-CoTAPc, CoHFPc, CoCOOHPc, CoOBuPc, and the catalase that is a hydrogen-peroxide dialytic ferment as a catalyst B as a production electrochemistry catalyst A of test electrodes 61, 62, 63, 64, 65, and 66.
[0085] It replaced with MnOOH used for test electrodes 21, 31, 41, and 51 as a catalyst B, and test electrodes 61, 62, 63, and 64 were produced by the same approach as the production approach of test electrodes 21, 31, 41, and 51 except having used the catalase.
[0086] Moreover, the test electrode 65 was produced by the same approach as the production approach of a test electrode 14 except having replaced with MnOOH used as a catalyst B of a test electrode 14, and having used the catalase.
[0087] Moreover, the test electrode 66 was produced by the same approach as the production approach of a test electrode 15 except having replaced with MnOOH used as a catalyst B of a test electrode 15, and having used the catalase.
[0088] (12) 3 pole cel which uses as a working electrode the test electrode produced at the process beyond evaluation of the oxygen reduction property of a test electrode, and uses a counter electrode and an Ag/AgCl (saturation KCl) electrode as a reference electrode for platinum was constituted, and the reduction property of oxygen was evaluated. The 0.1M phosphoric acid buffer solution of pH7.4 was used for the electrolytic solution. Electrolysis was performed after dissolved oxygen was saturated [be / it / under / during 30 minutes / electrolytic-solution / leading] in oxygen gas. The potential of a working electrode was increased at the rate of 50 mV/s toward 0V, when it decreased at the rate of 50 mV/s from +0.1V to -1.2V to the reference electrode and having been amounted to -1.2V, and the electrolytic current which flows between a working electrode and counter electrodes was recorded to the potential of a working electrode at this time.
[0089] In the test electrodes 61, 62, 63, and 64 according to this invention which compound-ized the electrochemistry catalyst A and Catalyst B, the twice [about] as many oxygen reduction peak current value as this was given compared with the test electrodes 22, 32, 42, and 52 which do not include Catalyst B. The summit potential (Ep) of the reduction current corresponding to the reduction reaction of oxygen is shown in Table 1. The reduction potential of oxygen is shifted to a plus-in -0.75V to -0.35--0.05V side, and can return oxygen by electropositive potential more.
[0090] Next, the controlled potential electrolysis was continuously performed with each summit potential (Ep) about each of test electrodes 61, 62, 63, 64, 65, and 66. The Ist value 200 seconds after a controlled potential electrolysis is shown in Table 1. A stationary current value is 18-30microA in the test electrodes 61, 62, 63, 64, 65, and 66 according to this invention. Compared with the test electrodes 22, 32, 42, and 52 which do not include Catalyst B, the twice [about] as many stationary current value as this was given, and oxygen was seemingly returned with the selectivity near about 100% at 4 electronic reactions.
[0091] (Example 7)
(13) The test electrode was produced using GC with a same diameter [the / as an example 1] of 6mm as a production electrochemistry catalyst A of test electrodes 71, 72, 73, 74, 75, and 76, using perovskite oxide La0.8Sr0.2MnO3 as p-CoTAPc, CoHFPc, CoCOOHPc, CoOBuPc, and a catalyst B.
[0092] It replaced with MnOOH used for test electrodes 21, 31, 41, and 51 as a catalyst B, and test electrodes 71, 72, 73, and 74 were produced by the same approach as the production approach of test electrodes 21, 31, 41, and 51 except having used La0.8Sr0.2MnO3.
[0093] Moreover, it replaced with MnOOH used for the test electrode 14 as a catalyst B, and the test electrode 75 was produced by the same approach as the production approach of a test electrode 14 except having used La0.8Sr0.2MnO3.
[0094] Moreover, it replaced with MnOOH used for the test electrode 15 as a catalyst B, and the test electrode 76 was produced by the same approach as the production approach of a test electrode 15 except having used La0.8Sr0.2MnO3.
[0095] (14) 3 pole cel which uses as a working electrode the test electrode produced according to the evaluation above-mentioned process of the oxygen reduction property of a test electrode, and uses a counter electrode and an Ag/AgCl (saturation KCl) electrode as a reference electrode for platinum was constituted, and the reduction property of oxygen was evaluated. The 0.1M phosphoric acid buffer solution of pH7.4 was used for the electrolytic solution. Electrolysis was performed after dissolved oxygen was saturated [be / it / under / electrolytic-solution / leading] for 30 minutes in oxygen gas. The potential of a working electrode was increased at the rate of 50 mV/s toward 0V, when it decreased at the rate of 50 mV/s from +0.1V to -1.2V to the reference electrode and having been amounted to -1.2V, and the electrolytic current which flows between a working electrode and counter electrodes was recorded to the potential of a working electrode at this time.
[0096] In the test electrodes 71, 72, 73, 74, 75, and 76 according to this invention which compound-ized the electrochemistry catalyst A and Catalyst B, the twice [about] as many oxygen reduction peak current value as this was given compared with the test electrodes 22, 32, 42, and 52 which do not include Catalyst B. The summit potential (Ep) of the reduction current corresponding to the reduction reaction of oxygen is shown in Table 1. The reduction potential of oxygen is shifted to a plus-in -0.75V to -0.40--0.10V side, and can return oxygen by electropositive potential more.
[0097] Next, the controlled potential electrolysis was continuously performed with each summit potential (Ep) about each of test electrodes 71, 72, 73, 74, 75, and 76. The Ist value 200 seconds after a controlled potential electrolysis is shown in Table 1. A stationary current value is 16-28microA in the test electrodes 71, 72, 73, 74, 75, and 76 according to this invention. Compared with the test electrodes 22, 32, 42, and 52 which do not include Catalyst B, the twice [about] as many stationary current value as this was given, and oxygen was seemingly returned with the selectivity near about 100% at 4 electronic reactions.
[0098] The test electrode which replaces a part and is equivalent to test electrodes 71-74 is produced. in addition, it is all in iron (Fe) and manganese (Mn) about the cobalt (Co) of a central metal -- it is -- the effectiveness as the test electrode using the metal complex of cobalt (Co) that a central metal is almost the same when an oxygen reduction property is evaluated, i.e., the reduction potential of oxygen, -- ** (plus) -- it shifted to the direction and the twice [about] as many peak current value as this and the stationary current value were acquired.
[0099] (Example 8)
(13) The generation-of-electrical-energy cel A of a configuration of being shown in assembly drawing 3 of a generation-of-electrical-energy cel and the generation-of-electrical-energy cel B were assembled.
[0100] In the generation-of-electrical-energy cel A, the air pole (6) which act as a positive electrode embed the mixture which become ** 3 from the Mn2O3 powder 2 weight section which installed the cobalt tetra-carboxy phthalocyanine (CoCOOHPc) which showed the structure expression 2.0% of the weight, the activated carbon powder 1 weight section, the acetylene black powder 0.3 weight section, and the polytetrafluoroethylene (PTFE) binder 0.2 weight section on a nickel screen with a thickness of 0.2mm, made it hold, and be produced.
[0101] The photocatalyst electrode which acts as a negative electrode consisted of glass substrate (1) ITO thin film (2) TiO2 particle film (3) and a coloring matter molecule. The light transmission nature conductivity substrate with which the indium and the stannic

acid ghost (ITO) thin film of 10 ohms / ** (2) were formed for surface electrical resistance on the glass substrate (1) with a thickness of 1mm was prepared, and the acetonitrile solution which contains the polyethylene glycol which distributed TiO_2 particle whose mean diameter is 10nm 11% of the weight 30% of the weight was applied on the ITO thin film by dip coating. After drying this at 80 degrees C, the TiO_2 particle film (3) with a thickness of about 10 micrometers was formed by heating at 400 degrees C in air for 1 hour. Next, the coloring matter molecule was installed on the TiO_2 particle film by being immersed into the ethanol which carried out 10mM dissolution of the ruthenium metal complex coloring matter molecule which showed structure to ** 5 for the TiO_2 particle film. Furthermore, the photocatalyst electrode was produced by drying it, after being immersed in a 4-tert-butyl pyridine, and washing this by the acetonitrile. In addition, 12 is a sealing agent which consists of silicone rubber of transparence.

[0102]

[Formula 5]



[0103] What carried out the glucose as the electrolytic solution and fuel liquid (5) at 0.1MKOH water solution, and carried out 5mM dissolution of 50mM(s) and the NADH as a carbohydrate was used. The electrolytic solution and fuel liquid (5) are poured in from the electrolytic solution and a fuel liquid inlet (8a), and is discharged from an exhaust port (8b) after a generation of electrical energy. Air is supplied to the interior of a generation-of-electrical-energy cel from the exterior through the oxygen permeability hydrofuge film (7).

[0104] Except having used the air pole using Mn_2O_3 which does not install CoCOOHPc, the generation-of-electrical-energy cel B was produced so that it might become the same configuration as the generation-of-electrical-energy cel A.

[0105] A photocatalyst electrode generates optical active species (S+) and an electron by optical exposure. S+ returns an electron from NADH (reductant) to reception and the original ground state kind (S). NADH which passed the electron serves as an oxidant (NAD+), and this NAD+ oxidizes the glucose ($C_6H_{12}O_6$) which is a fuel, and returns an electron from a glucose to reception NADH. The electron generated with the photocatalyst electrode reaches the oxygen pole which is a positive electrode through an external circuit, and is used for the reduction reaction of oxygen (O_2). The following reaction formulae show the above generation-of-electrical-energy reaction.

<Negative electrode> S -> S+ + e - (to external circuit)

NADH + S+ -> NAD+ + S NAD+ + $C_6H_{12}O_6$ -> NADH + $C_6H_{11}O_6$ + H+ (to positive electrode)

<Positive electrode> 1 / $2O_2$ + e- (from an external circuit) + H+(from negative electrode) -> 1/$2H_2O$ <a whole reaction> $C_6H_{12}O_6$ + 1 / $2O_2$ -> $C_6H_{11}O_6$ + 1/$2H_2O$ [0106] (14) After filling with the electrolytic solution and fuel liquid the generation-of-electrical-energy cel produced according to the operating-characteristic above-mentioned process of a generation-of-electrical-energy cel, the light from a sunlight simulator (AM1.5, 100 mW/cm2) was irradiated from the glass substrate (1) side, and the electrical potential difference of a generation-of-electrical-energy cel at the time of discharging for 20 minutes with the electromotive force (OCV) of a generation-of-electrical-energy cel and the fixed current of 100microA was measured. OCV was 1.20V in 1.30V and the generation-of-electrical-energy cel B in the generation-of-electrical-energy cel A. Moreover, the electrical potential difference of the generation-of-electrical-energy cel after discharge was 1.0V in 1.20V and the generation-of-electrical-energy cel B for 20 minutes in the generation-of-electrical-energy cel A.

[0107] In the generation-of-electrical-energy cel A which has the oxygen reduction composite electrode of this invention, while high electromotive force was acquired compared with the generation-of-electrical-energy cel B, even if it faced discharge, the high electrical potential difference was maintainable.

[0108] (Example 9)

(Fuel cell) The oxygen reduction composite electrode of this invention can be used for an air pole, a negative electrode can be used as a fuel electrode, an air pole and a fuel electrode can be connected through the ion exchange membrane of proton conductivity, and a fuel cell can be constituted.

[0109] Drawing 4 is the mimetic diagram showing an example of the structure of a fuel cell. The single cel 20 of a fuel cell is connected through the electrolyte 23 of proton conductivity [fuel electrode / 22 / an air pole 21 and]. To an air pole 21, air is supplied from the air supply opening 24, and it is exhausted from the air exhaust port 25 after a reaction. On the other hand, to a fuel electrode 22, the fuel gas which contains hydrogen from the fuel feed hopper 26 is supplied, and it is exhausted from the fuel exhaust port 27 after a reaction. Here, the following reaction formulae show a generation-of-electrical-energy reaction.

<Negative electrode> H_2 -> 2H+ + 2e - (to external circuit)

<Positive electrode> 1 / $2O_2$ + 2H+ + 2e- (from an external circuit) -> H_2O [0110] The sheet-like air pole which kneads the mixture which consists of the Mn_2O_3 powder 2 weight section which installed the cobalt tetra-carboxy phthalocyanine (CoCOOHPc) which showed the structure expression 2.0% of the weight, the activated carbon powder 1 weight section, the acetylene black powder 0.3 weight section, and the PTFE binder 0.2 weight section to ** 3, rolls out to it, and grows into it can be used for an air pole. On the other hand, the sheet-like fuel electrode which rolls [adds a PTFE binder, kneads and] out and grows into the carbon particle which made the platinum of the specified quantity support can be used for a fuel electrode. Subsequently, for example, a sheet-like air pole and a sheet-like fuel electrode are stuck to both sides of the proton conductivity ion exchange membrane of Nafion 112 grade by pressure, it unites with them, and a single cel is produced. Or apply liquefied ion exchange membrane to one side of an air pole and a

fuel electrode, and it is made to dry and solidify it, and an air pole and a fuel electrode can be stuck by pressure, and it can also be made to unify through the solidified ion exchange membrane after that. In addition, two or more laminatings of the cell produced by the above-mentioned approach can be carried out, and a stack can also be constituted.
[0111] By using the oxygen reduction composite electrode of this invention for a positive electrode, electromotive force and a fuel cell with the high cell voltage at the time of discharge can be obtained compared with the former.
[0112] (Example 10)
(Air cell) An air cell can be constituted by using the oxygen reduction composite electrode of this invention for a positive electrode, and using metals, such as zinc, magnesium, and aluminum, for a negative electrode. For example, the air zinc cell which used zinc for the negative electrode is producible by the following approaches.
[0113] drawing 5 shows an example of the structure of an air cell -- it is a notching sectional view a part. The laminating of the oxygen permselective membrane 35, the water-repellent film 34, an air pole 31, and the separator 33 is carried out to the metal positive-electrode case 37 where it has a vent 36 at the pars basilaris ossis occipitalis, one by one from the base side. On the other hand into the metal negative-electrode case 38, zinc powder, a gelling agent, and the negative electrode 32 containing the alkali electrolytic solution are held, and it insulates and obturates the positive-electrode case 37 and the negative-electrode case 38 through the gasket 39. 40 is an adhesion seal which closes a vent 36. Here, the water-repellent film plays the role which prevents the oxygen supply to an air pole, and the liquid spill to the cell exterior of the electrolytic solution. In addition, the following reaction formulae show a generation-of-electrical-energy reaction.
<Negative electrode> Zn + 2OH- -> Zn2 (OH) + 2e - (to external circuit)
<Positive electrode> 1 / 2O2 +H2O +2e- (from an external circuit) -> 2OH-[0114] What the air pole which acts as a positive electrode was made to embed and hold the mixture which becomes ** 3 from the Mn2O3 powder 2 weight section which installed the cobalt tetra-carboxy phthalocyanine (CoCOOHPc) which showed the structure expression 2.0% of the weight, the activated carbon powder 1 weight section, the acetylene black powder 0.3 weight section, and the PTFE binder 0.2 weight section on a nickel screen with a thickness of 0.2mm, and produced it to it can be used.
[0115] Next, the laminating of oxygen permselective membrane, the water-repellent film, an air <DP N=0014> pole, and the separator is carried out to the metal positive-electrode case where it has a vent at the pars basilaris ossis occipitalis, one by one from a base side. On the other hand, the negative electrode which contains zinc powder, a gelling agent, and the alkali electrolytic solution as a negative-electrode active material is held in a metal negative-electrode case. Subsequently, a positive-electrode case and a negative-electrode case are insulated and sealed through a gasket.
[0116] By using the oxygen reduction composite electrode of this invention for a positive electrode, electromotive force and the cell voltage at the time of discharge can obtain an air cell high about 0.5v from 0.1V compared with the former.
[0117] In addition, although this example 10 showed the example which used zinc to the negative electrode, when replacing with zinc and using magnesium or aluminum, it can produce by the same approach as this example 10, and has the same effectiveness.
[0118]
[Effect of the Invention] According to this invention, the oxygen reduction composite electrode which is used for an oxygen pole or an air pole of electrochemistry devices, such as fuel cells, such as air cells, such as a zinc-air cell using the reduction reaction of oxygen as a positive-electrode reaction, an aluminum-air cell, and a sugar-air cell, and an oxygen hydrogen fuel cell, a methanol fuel cell, etc. and which was excellent also in the stability which gives 4 electronic reduction reaction with the selectivity near 100% seemingly to electrochemistry reduction of oxygen is offered.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is drawing showing the current-electrical-potential-difference response characteristic of the electrode of this invention.
[Drawing 2] It is drawing showing the current-time response at the time of the controlled potential electrolysis of the electrode of this invention.
[Drawing 3] It is the type section Fig. showing the structure of the generation-of-electrical-energy cel of one example of this invention.

[Drawing 4] It is the mimetic diagram showing the structure of the fuel cell of one example of this invention.
[Drawing 5] the structure of the air cell of one example of this invention is shown -- it is a notching sectional view a part.
[Description of Notations]
1 Glass Substrate, 2 ITO Thin Film, 3 TiO2 Particle Thin Film, 4 A coloring matter molecular layer, 5 The electrolytic solution and fuel liquid, 6 An air pole, 7 Oxygen permeability hydrofuge film, 8a The electrolytic solution and a fuel liquid inlet, 8b The electrolytic solution and a fuel liquid exhaust port, 9a, 9b Liquid bulb, 10 A negative-electrode lead, 11 A positive-electrode lead, 12 A sealing agent, 20 The single cel of a fuel cell, 21 An air pole, 22 A fuel electrode, 23 An electrolyte, 24 Air supply opening, 25 An air exhaust port, 26 A fuel feed hopper, 27 A fuel exhaust port, 30 Air cell, 31 An air pole, 32 A negative electrode, 33 A separator, 34 The water-repellent film, 35 Oxygen permselective membrane, 36 A vent, 37 A positive-electrode case, 38 A negative-electrode case, 39 A gasket, 40 Pressure sensitive adhesive sheet.

[Translation done.]

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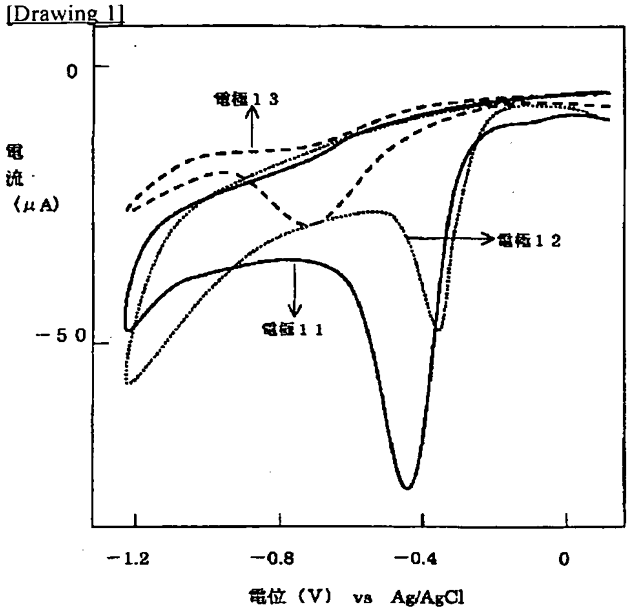
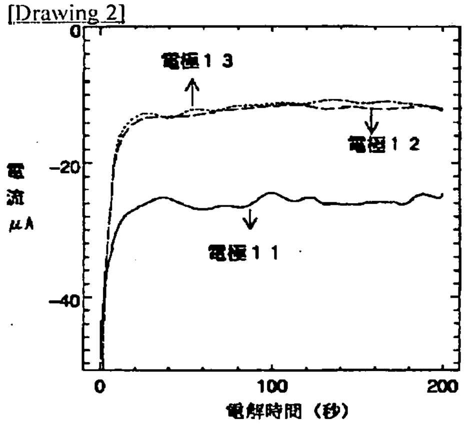
DRAWINGS

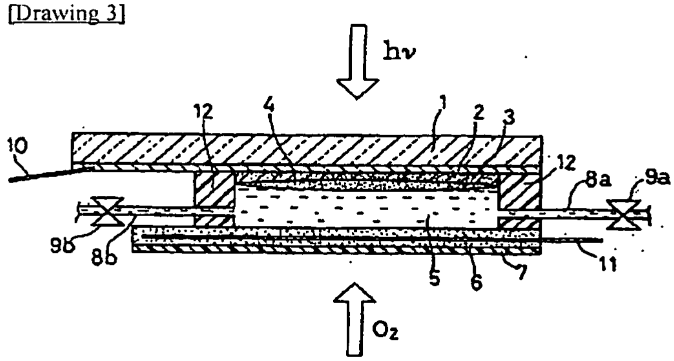
[Drawing 1]



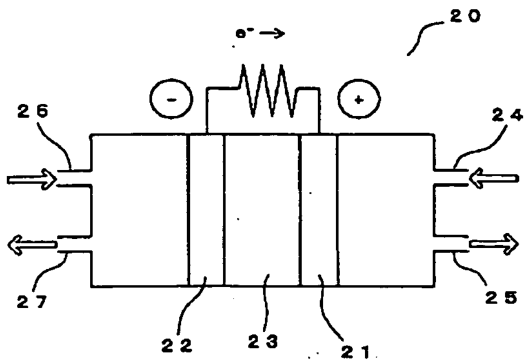
[Drawing 2]



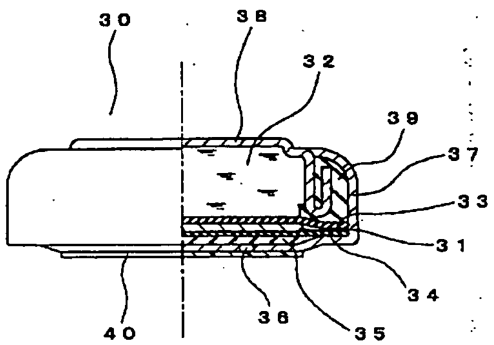
[Drawing 3]



[Drawing 4]



[Drawing 5]



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CORRECTION OR AMENDMENT

[Kind of official gazette] Printing of amendment by the convention of 2 of Article 17 of Patent Law
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H01M 12/06

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H01M 12/06 F

[Procedure revision]
[Filing Date] January 18, Heisei 17 (2005. 1.18)
[Procedure amendment 1]
[Document to be Amended] Specification
[Item(s) to be Amended] Claim
[Method of Amendment] Modification
[The contents of amendment]
[Claim(s)]
[Claim 1]
The electrochemistry catalyst A which carries out the catalyst of the 2 electronic reduction reaction which generates a hydrogen peroxide by electrochemistry reduction of oxygen
It is the composite electrode for oxygen reduction which contains the catalyst B which carries out the catalyst of the decomposition reaction which disassembles the generated hydrogen peroxide and generates oxygen at least,
The electrode potential of the above-mentioned composite electrode is the oxygen reduction potential of the electrochemistry catalyst A, and the electrochemistry catalyst A returns two electrons of oxygen reproduced by Catalyst B decomposing a hydrogen peroxide, and it repeats and generates a hydrogen peroxide,
The above-mentioned electrochemistry catalyst A and Catalyst B are held at a conductive base material, and change,
The composite electrode for oxygen reduction which insulates Catalyst B electrically and changes so that an electron may not move through direct or an electronic conductor between the above-mentioned catalyst B, a conductive base material, and/or the electrochemistry catalysts A.
[Claim 2]
The composite electrode for oxygen reduction according to claim 1 which is the metal complex which has the ligand L configurated in the central metal atom alpha by which the above-mentioned electrochemistry catalyst A is expressed with alphaLn (the number of the ligands which n configurates), and this metal atom alpha.
[Claim 3]
The composite electrode for oxygen reduction according to claim 2 whose ligand of the above-mentioned metal complex is the single seat which has a nitrogen atom, or a multidentate ligand.
[Claim 4]
The composite electrode for oxygen reduction according to claim 3 with which the above-mentioned ligand has a porphyrin ring or a phtalo cyanogen ring.
[Claim 5]
The composite electrode for oxygen reduction according to claim 4 with which the above-mentioned Pori Phi Lynne ring or an above-mentioned phtalo cyanogen ring has the substituent of polymerization nature.
[Claim 6]
The composite electrode for oxygen reduction according to claim 1 which is the metallic oxide by which the above-mentioned catalyst B is expressed with a hydrogen-peroxide dialytic ferment or betaOx (atomic number of the oxygen beta is decided by the metallic element and it is decided with the valence of a metallic element that x will be).
[Claim 7]
The composite electrode for oxygen reduction according to claim 6 whose above-mentioned metallic oxide is a manganic acid ghost expressed with a perovskite oxide or MnOy (atomic number of the oxygen it is decided with the valence of manganese that y will be).

[Claim 8]
a metallic material, a carbon material, a metallic oxide, and the metal complex that has the ligand L configurated in the central metal atom alpha expressed with alphaLn (the number of the ligands which n configurates), and this metal atom alpha -- since -- the electrochemistry catalyst A which carries out the catalyst of the 2 electronic reduction reaction which is one sort chosen from the group which changes, and generates a hydrogen peroxide by the electrochemical reduction of oxygen
It consists of the metallic oxide expressed with a hydrogen-peroxide dialytic ferment or betaOx (atomic number of the oxygen beta is decided by the metallic element and it is decided with the valence of a metallic element that x will be), and the catalyst B which carries out the catalyst of the decomposition reaction which disassembles the hydrogen peroxide generated according to the electrochemistry catalyst A, and generates oxygen is included at least,
The above-mentioned electrochemistry catalyst A and Catalyst B are held at a conductive base material, and change,
The composite electrode for oxygen reduction which insulates Catalyst B electrically and changes so that an electron may not move through direct or an electronic conductor between the above-mentioned catalyst B, a conductive base material, and/or the electrochemistry catalysts A.
[Claim 9]
The composite electrode for oxygen reduction according to claim 8 with which the above-mentioned electrochemistry catalyst A serves as a conductive base material.
[Claim 10]
The oxygen reduction composite electrode according to claim 8 with which the polymer of proton conductivity distributes and the above-mentioned catalyst B changes.
[Claim 11]
The above-mentioned electrochemistry catalyst is a metal complex which has the ligand L configurated in the central metal atom alpha expressed with alphaLn (the number of the ligands which n configurates), and this metal atom alpha,
The composite electrode for oxygen reduction according to claim 8 whose ligand of the above-mentioned metal complex is the single seat which has a nitrogen atom, or a multidentate ligand.
[Claim 12]
The composite electrode for oxygen reduction according to claim 11 with which the above-mentioned ligand has a porphyrin ring or a phthalocyanine ring.
[Claim 13]
The composite electrode for oxygen reduction according to claim 12 with which the above-mentioned Pori Phi Lynne ring or an above-mentioned phtalo cyanogen ring has the substituent of polymerization nature.
[Claim 14]
The above-mentioned catalyst B consists of a metallic oxide expressed with betaOx (atomic number of the oxygen beta is decided by the metallic element and it is decided with the valence of a metallic element that x will be),
The composite electrode for oxygen reduction of any one publication of 13 from claim 8 whose above-mentioned metallic oxide is a manganic acid ghost expressed with a perovskite oxide or MnOy (atomic number of the oxygen it is decided with the valence of manganese that y will be).
[Claim 15]
The above-mentioned metallic oxide is a perovskite oxide,
The composite electrode for oxygen reduction according to claim 14 whose above-mentioned perovskite oxide is LaxSr1-xMnO3 (x=0-0.5).
[Claim 16]
It consists of the composite electrode for oxygen reduction which contains the catalyst B which carries out the catalyst of the decomposition reaction which disassembles the electrochemistry catalyst A which carries out the catalyst of the 2 electronic reduction reaction which generates a hydrogen peroxide by electrochemistry reduction of oxygen, and the generated hydrogen peroxide, and generates oxygen at least,
The electrode potential of the above-mentioned composite electrode is the oxygen reduction potential of the electrochemistry catalyst A,
The positive electrode which the electrochemistry catalyst A returns two electrons of oxygen reproduced by Catalyst B decomposing a hydrogen peroxide, and repeats and generates a hydrogen peroxide,
The negative electrode which carries out oxidation reaction of a negative-electrode active material or the fuel matter,
Electrolyte,
It is the generation-of-electrical-energy cel which ****,
The above-mentioned electrochemistry catalyst A and Catalyst B are held at a conductive base material, and change,
The generation-of-electrical-energy cel which insulates Catalyst B electrically and changes so that an electron may not move through direct or an electronic conductor between the above-mentioned catalyst B, a conductive base material, and/or the electrochemistry catalysts A.
[Claim 17]
The generation-of-electrical-energy cel according to claim 16 which consists of the metal complex which has the ligand L configurated in the central metal atom alpha by which the above-mentioned electrochemistry catalyst A is expressed with alphaLn (the number of the ligands which n configurates), and this metal atom alpha, and consists of the metallic oxide by which the above-mentioned catalyst B is expressed with a hydrogen-peroxide dialytic ferment or betaOx (atomic number of the oxygen beta is decided by the metallic element and it is decided with the valence of a metallic element that x will be).
[Claim 18]
It consists of the composite electrode for oxygen reduction which contains the catalyst B which carries out the catalyst of the decomposition reaction which disassembles the electrochemistry catalyst A which carries out the catalyst of the 2 electronic reduction reaction which generates a hydrogen peroxide by electrochemistry reduction of oxygen, and the generated hydrogen peroxide, and generates oxygen at least,
The electrode potential of the above-mentioned composite electrode is the oxygen reduction potential of the electrochemistry catalyst A,
The positive electrode which the electrochemistry catalyst A returns two electrons of oxygen reproduced by Catalyst B decomposing a hydrogen peroxide, and repeats and generates a hydrogen peroxide,
The negative electrode which carries out oxidation reaction of a negative-electrode active material or the fuel matter,
Electrolyte,

It is the drive approach of a generation-of-electrical-energy cel of ****(ing),
The above-mentioned electrochemistry catalyst A and Catalyst B are held at a conductive base material, and change,
Catalyst B is insulated electrically and it changes so that an electron may not move through direct or an electronic conductor between the above-mentioned catalyst B, a conductive base material, and/or the electrochemistry catalysts A,
The drive approach of the above-mentioned generation-of-electrical-energy cel,
The molecule which is excited by light absorption and oxidizes a carbohydrate electrochemically is given to either [at least] the above-mentioned negative electrode or the electrolyte,
The drive approach of a generation-of-electrical-energy cel of supplying a carbohydrate to this molecule with Mitsuteru putting, making a carbohydrate oxidizing with this molecule in a negative electrode, and having the process which generates electromotive force between a positive electrode and a negative electrode.
[Claim 19]
The generation-of-electrical-energy cel according to claim 16 which the above-mentioned generation-of-electrical-energy cel is a fuel cell, the above-mentioned positive electrode and a negative electrode are used as an air pole and a fuel electrode, respectively, and an air pole and a fuel electrode are connected through the ion exchange membrane of proton conductivity, and changes.
[Claim 20]
The generation-of-electrical-energy cel according to claim 16 using the gap or one sort of metals which the above-mentioned generation-of-electrical-energy cel is an air cell, and be chosen as the above-mentioned negative electrode from zinc, magnesium, and aluminum.
[Procedure amendment 2]
[Document to be Amended] Specification
[Item(s) to be Amended] 0007
[Method of Amendment] Modification
[The contents of amendment]
[0007]
[Means for Solving the Problem]
In order to solve an above-mentioned technical problem the composite electrode for oxygen reduction of this invention The electrochemistry catalyst A which carries out the catalyst of the 2 electronic reduction reaction which generates a hydrogen peroxide by electrochemistry reduction of oxygen It is the composite electrode for oxygen reduction which contains the catalyst B which carries out the catalyst of the decomposition reaction which disassembles the generated hydrogen peroxide and generates oxygen at least. The electrode potential of the above-mentioned composite electrode is the oxygen reduction potential of the electrochemistry catalyst A. The electrochemistry catalyst A returns two electrons of oxygen reproduced by Catalyst B decomposing a hydrogen peroxide, a hydrogen peroxide is repeated and generated, and the above-mentioned electrochemistry catalyst A and Catalyst B are held at a conductive base material, and change. The above-mentioned catalyst B It is characterized by insulating Catalyst B electrically and changing so that an electron may not move between a conductive base material and/or the electrochemistry catalysts A through direct or an electronic conductor.
[Procedure amendment 3]
[Document to be Amended] Specification
[Item(s) to be Amended] 0013
[Method of Amendment] Deletion
[The contents of amendment]

[Procedure amendment 4]
[Document to be Amended] Specification
[Item(s) to be Amended] 0014
[Method of Amendment] Modification
[The contents of amendment]
[0014]
Preferably, it is that Catalyst B is distributed by the polymer of proton conductivity.
[Procedure amendment 5]
[Document to be Amended] Specification
[Item(s) to be Amended] 0020
[Method of Amendment] Modification
[The contents of amendment]
[0020]
A generation-of-electrical-energy cel can be constituted by using the composite electrode for oxygen reduction of this invention as the positive electrode of an air cell which considers the reduction reaction of oxygen as a positive-electrode reaction, or a positive electrode of a fuel cell.
Namely, the electrochemistry catalyst A which carries out the catalyst of the 2 electronic reduction reaction whose this invention generates a hydrogen peroxide by electrochemistry reduction of oxygen The catalyst B which carries out the catalyst of the decomposition reaction which disassembles the generated hydrogen peroxide and generates oxygen Even if few, it consists of the composite electrode for oxygen reduction to contain, and the electrode potential of the above-mentioned composite electrode is the oxygen reduction potential of the electrochemistry catalyst A. The positive electrode which the electrochemistry catalyst A returns two electrons of oxygen reproduced by Catalyst B decomposing a hydrogen peroxide, and repeats and generates a hydrogen peroxide, It has the negative electrode which carries out oxidation reaction of a negative-electrode active material or the fuel matter, and an electrolyte, and the above-mentioned electrochemistry catalyst A and Catalyst B are held at a conductive base material, and change. The above-mentioned catalyst B The generation-of-electrical-energy cel which insulates Catalyst B electrically and changes is offered so that an electron may not move between a conductive base material and/or the electrochemistry catalysts A through direct or an electronic conductor.
[Procedure amendment 6]
[Document to be Amended] Specification
[Item(s) to be Amended] 0105
[Method of Amendment] Modification .
[The contents of amendment]

[0105]
A photocatalyst electrode generates optical active species (S+) and an electron by optical exposure. S+ returns an electron from NADH (reductant) to reception and the original ground state kind (S). NADH which passed the electron serves as an oxidant (NAD+), and this NAD+ oxidizes the glucose (C6H12O6) which is a fuel, and returns an electron from a glucose to reception NADH. The electron generated with the photocatalyst electrode reaches the oxygen pole which is a positive electrode through an external circuit, and is used for the reduction reaction of oxygen (O2). The following reaction formulae show the above generation-of-electrical-energy reaction.

<Negative electrode>
S -> S+ + e - (to external circuit)
NADH + S+ -> NAD+ + S
NAD+ + C6H12O6 ->
NADH + C6H11O6 + H+ (to positive electrode)

<Positive electrode>
1 / 2O2 + 2e- (from an external circuit) + 2H+(from negative electrode) ->
H2O
<Whole reaction>
2C6H12O6 + 1 / 2O2 -> 2C6H11O6 + H2O

[Translation done.]

COMPOUND ELECTRODE FOR OXYGEN REDUCTION

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Applicant: MATSUSHITA ELECTRIC IND CO LTD

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- european:

Application number: JP20020246983 20020827

Priority number(s): JP20020246983 20020827; JP20010259283 20010829

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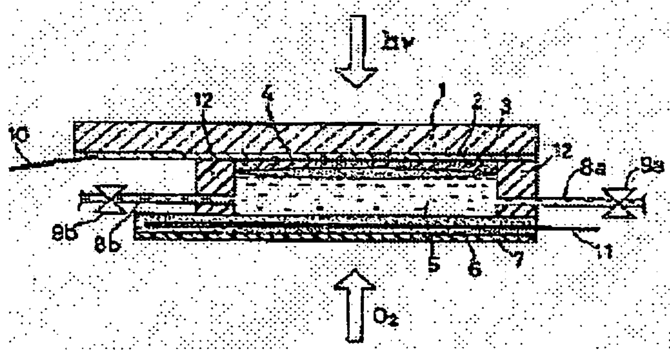
Abstract of **JP2003151567**

PROBLEM TO BE SOLVED: To provide an oxygen reduced compound electrode to which 4-electron reduction reaction is seemingly given at the rate of selection near 100% to electrochemical reduction of oxygen. SOLUTION: The oxygen reducted compound electrode is constituted so that at least an electrochemical catalyst A, which catalyzes the 2-electrons reduction reaction, which generates hydrogen peroxide by electrochemical reduction of oxygen, and the catalyst B, which catalyzes the decomposition reaction, which decomposes the generated hydrogen peroxide, and generates oxygen, may be contained. By making the electrode potential of the compound electrode for oxygen reduction as the oxygen reduction potential of the electrochemical catalyst A, the electrochemical catalyst A carries out 2-electrons reduction to the oxygen reproduced by decomposing hydrogen peroxide by the catalyst B, then, the hydrogen peroxide is generated repeatedly.



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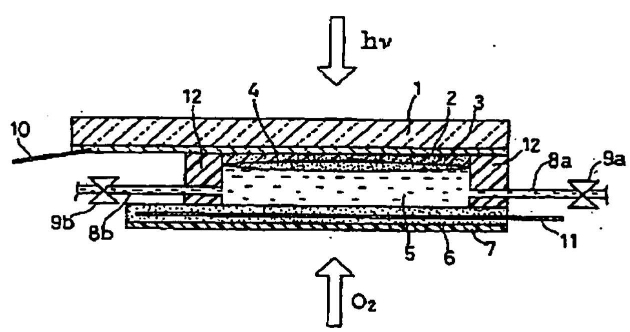
最終頁に続く

(54)【発明の名称】　酸素還元用複合電極

(57)【要約】
【課題】　酸素の電気化学還元に対して、見かけ上、４電子還元反応を１００％に近い選択率で与えられる酸素還元複合電極を提供することを目的とする。
【解決手段】　少なくとも、酸素の電気化学還元により過酸化水素を生成する２電子還元反応を触媒する電気化学触媒Ａと、生成した過酸化水素を分解して酸素を生成する分解反応を触媒する触媒Ｂとを含有するように酸素還元複合電極を構成する。酸素還元用複合電極の電極電位を電気化学触媒Ａの酸素還元電位として、触媒Ｂにより過酸化水素を分解して再生された酸素を、電気化学触媒Ａが２電子還元して、過酸化水素を繰返し生成させる。



【特許請求の範囲】

【請求項１】　酸素の電気化学還元により過酸化水素を生成する２電子還元反応を触媒する電気化学触媒Ａと、生成した過酸化水素を分解して酸素を生成する分解反応を触媒する触媒Ｂとを少なくとも含有する酸素還元用複合電極であって、

上記の複合電極の電極電位は電気化学触媒Ａの酸素還元電位であり、触媒Ｂにより過酸化水素を分解して再生された酸素を、電気化学触媒Ａが２電子還元して過酸化水素を繰返し生成する酸素還元用複合電極。

【請求項２】　上記電気化学触媒ＡがαL_n（ｎは配位する配位子の数）で表される中心金属原子αと、該金属原子αに配位する配位子Ｌとを有する金属錯体である請求項１記載の酸素還元用複合電極。

【請求項３】　上記金属錯体の配位子が、窒素原子を有する単座あるいは多座配位子である請求項２記載の酸素還元用複合電極。

【請求項４】　上記配位子が、ポルフィリン環又はフタロシアン環を有する請求項３記載の酸素還元用複合電極。

【請求項５】　上記のポリフィリン環又はフタロシアン環が、重合性の置換基を有する請求項４記載の酸素還元用複合電極。

【請求項６】　上記触媒Ｂが過酸化水素分解酵素又はβO_x（βは金属元素、ｘは金属元素の価数によって決まる酸素の原子数）で表される金属酸化物である請求項１から５のいずれか一つに記載の酸素還元用複合電極。

【請求項７】　上記金属酸化物が、ペロブスカイト酸化物又はMnO_y（ｙはマンガンの価数によって決まる酸素の原子数）で表されるマンガン酸化物である請求項６記載の酸素還元用複合電極。

【請求項８】　金属材料、炭素材料、金属酸化物、そしてαL_n（ｎは配位する配位子の数）で表される中心金属原子αと該金属原子αに配位する配位子Ｌとを有する金属錯体、から成る群から選択された１種であり、酸素の電気化学的還元により過酸化水素を生成する２電子還元反応を触媒する電気化学触媒Ａと、過酸化水素分解酵素又はβO_x（βは金属元素、ｘは金属元素の価数によって決まる酸素の原子数）で表される金属酸化物から成り、電気化学触媒Ａにより生成した過酸化水素を分解して酸素を生成する分解反応を触媒する触媒Ｂと、を少なくとも含む酸素還元用複合電極。

【請求項９】　上記電気化学触媒Ａと触媒Ｂとが、導電性基材に保持されて成る請求項８記載の酸素還元用複合電極。

【請求項１０】　上記電気化学触媒Ａが、導電性基材を兼ねる請求項９記載の酸素還元用複合電極。

【請求項１１】　上記触媒Ｂと、導電性基材及び／又は電気化学触媒Ａとの間を、直接もしくは電子伝導体を介して電子が移動しないように、触媒Ｂを電気的に絶縁して成る請求項９又は１０に記載の酸素還元用複合電極。

【請求項１２】　上記触媒Ｂが、プロトン導電性のポリマーに分散されて成る請求項１１記載の酸素還元複合電極。

【請求項１３】　上記金属錯体の配位子が、窒素原子を有する単座あるいは多座配位子である請求項８から１２のいずれか一つに記載の酸素還元用複合電極。

【請求項１４】　上記配位子が、ポルフィリン環又はフタロシアニン環を有する請求項１３記載の酸素還元用複合電極。

【請求項１５】　上記のポリフィリン環又はフタロシアン環が、重合性の置換基を有する請求項１４記載の酸素還元用複合電極。

【請求項１６】　上記金属酸化物が、ペロブスカイト酸化物又はMnO_y（ｙはマンガンの価数によって決まる酸素の原子数）で表されるマンガン酸化物である請求項８から１５のいずれか一つに記載の酸素還元用複合電極。

【請求項１７】　上記ペロブスカイト酸化物が、$La_x Sr_{1-x} MnO_3$（$x = 0 \sim 0.5$）である請求項１６記載の酸素還元用複合電極。

【請求項１８】　酸素の電気化学還元により過酸化水素を生成する２電子還元反応を触媒する電気化学触媒Ａと、生成した過酸化水素を分解して酸素を生成する分解反応を触媒する触媒Ｂと、を少なくとも含有する酸素還元用複合電極から成り、上記の複合電極の電極電位は電気化学触媒Ａの酸素還元電位であり、触媒Ｂにより過酸化水素を分解して再生された酸素を電気化学触媒Ａが２電子還元して過酸化水素を繰返し生成する正極と、負極活物質あるいは燃料物質の酸化反応をする負極と、電解質と、を有する発電セル。

【請求項１９】　上記電気化学触媒ＡがαL_n（ｎは配位する配位子の数）で表される中心金属原子αと、該金属原子αに配位する配位子Ｌとを有する金属錯体から成り、上記触媒Ｂが過酸化水素分解酵素又はβO_x（βは金属元素、ｘは金属元素の価数によって決まる酸素の原子数）で表される金属酸化物から成る請求項１８記載の発電セル。

【請求項２０】　上記負極及び電解質の少なくとも一方に、光吸収により励起されて炭水化物を電気化学的に酸化する分子を付与し、該分子に光照射しながら炭水化物を供給して、負極において該分子により炭水化物を酸化せしめて、正極と負極との間に起電力を発生させる請求項１８又は１９に記載の発電セル。

【請求項２１】　上記発電セルが燃料電池であり、上記正極及び負極を、それぞれ空気極と燃料極とし、空気極と燃料極とがプロトン導電性のイオン交換膜を介して接続されて成る請求項１８又は１９に記載の発電セル。

【請求項２２】　上記発電セルが空気電池であり、上記負極に亜鉛、マグネシウム及びアルミニウムから選択さ

れたいずれか１種の金属を用いる請求項１８又は１９に記載の発電セル。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、酸素を電極反応物質とする酸素還元複合電極に関する。特に、本発明の酸素還元複合電極は、酸素の還元反応を正極反応として用いる亜鉛―空気電池、アルミニウム―空気電池、砂糖―空気電池などの空気電池や、酸素水素燃料電池、メタノール燃料電池などの燃料電池など電気化学デバイスの酸素極あるいは空気極などに用いられる。

【０００２】

【従来の技術】従来、酸素（O_2）を電解還元すると、１電子還元ではスーパーオキシドの生成や、２電子還元では過酸化水素の生成、４電子還元では水が生成することが知られている（JACEK KIPKOWSKI, PHILIP N. ROSS 編集、ELECTROCATALYSIS、WILEY-VCH 出版、１９９８年、２０４－２０５頁）。酸素の還元反応を電池の正極反応として用い、大容量で、高電圧でしかも高電流の電池などの電気化学デバイスを得るには、できるだけ多くの電子移動を伴う酸素の電気化学還元反応を、できるだけ貴な（プラスの）電位で、しかも過電圧をできるだけ小さくして進行させることが必要である。

【０００３】すなわち、４電子還元反応を高電位でしかも過電圧を小さく起こすことのできる触媒が好ましい。このような触媒を得るためにこれまでいくつかの取り組みが報告されている。特公平２－３０１４１号公報、特公平２－３０１４２号公報には、酸素ガス還元能を有する鉄フタロシアニン、コバルトポルフィリンなどの金属キレート化合物を担持した導電性粉末と、フッ素樹脂の多孔質成形体とからなる触媒が提案されている。金属キレート化合物の２量体（二核錯体）を使うと、より高い酸素還元能（４電子還元能）が期待でき、大きな出力の空気電池が期待できると述べられている。

【０００４】コバルトポルフィリン二核錯体など、Ｃｒ，Ｍｎ，Ｆｅ，Ｃｏなどの遷移金属を中心金属とする大環状錯体を用いる酸素還元触媒の技術は、前述のELECTROCATALYSIS、WILEY-VCH 出版、１９９８年、２３２－２３４頁に述べられている。特開平１１－２５３８１１号公報には、酸素還元用二核マンガン錯体触媒が提案されている。この二核錯体は酸素の４電子還元反応を高い選択率で触媒する。マンガン原子は、２価から７価の価数をとりマイナス０．５Ｖからプラス２Ｖの電位範囲で酸素還元反応を触媒すると述べられている。

【０００５】

【発明が解決しようとする課題】しかしながら、どのような条件で、どのような触媒が酸素の1電子還元反応、２電子還元反応、４電子還元反応に有効なのかについては知られていない。４電子還元反応の選択率は錯体種により異なり、どのような金属錯体を用いれば、より高い４電子還元反応への選択率が安定して得られるのか、実際の利用にあたって必要とされる技術内容は知ることは困難である。さらに、これまで開示されている技術によれば、高い電位を得ようとすれば、価数の大きな中心金属原子を持つ二核金属錯体が必要で、このような二核金属錯体は、強い酸化力を有しており、実際の使用にあたって、このような二核金属錯体と一緒に用いられる電池の他の構成要素、例えば、電解液、電極リード、集電体、電池ケース、セパレータ、ガス選択透過膜などの酸化劣化をもたらすという難点がある。

【０００６】本発明は、このような問題を解決し、価数の大きな中心金属を持つ二核金属錯体などの酸化力の強い触媒成分を用いることなく、酸素の電気化学還元に対して、見かけ上、４電子還元反応を１００％に近い選択率で与える安定性にも優れた酸素還元複合電極を提供するものである。

【０００７】

【課題を解決するための手段】上述の課題を解決するため本発明の酸素還元用複合電極は、酸素の電気化学還元により過酸化水素を生成する２電子還元反応を触媒する電気化学触媒Ａと、生成した過酸化水素を分解して酸素を生成する分解反応を触媒する触媒Ｂとを少なくとも含有する酸素還元用複合電極であって、上記の複合電極の電極電位は電気化学触媒Ａの酸素還元電位であり、触媒Ｂにより過酸化水素を分解して再生された酸素を、電気化学触媒Ａが２電子還元して過酸化水素を繰返し生成することを特徴とする。

【０００８】本発明の酸素還元用複合電極は、少なくとも、酸素１分子を還元して過酸化水素１分子を生成させる酸素の２電子還元反応を行う電気化学触媒と、生成じた過酸化水素１分子を分解して酸素１／２分子を再生させる過酸化水素の分解反応を行う触媒と、を有しており、上記の２電子還元反応と上記の分解反応とを繰返し行うことにより、見かけ上、酸素の４電子還元を行うことができ、かつ、酸素の４電子還元反応を概ね１００％の選択率で行うことができる。ここで、酸素の４電子還元反応の選択率が概ね１００％であるとは、酸素の４電子還元反応以外の還元反応による電流が実質的に観測されないことを言う。

【０００９】上記電気化学触媒Ａは、αＬｎ（ｎは配位する配位子の数）で表される中心金属原子αと、該金属原子αに配位する配位子Ｌとを有する金属錯体であることが好ましくは、上記触媒ＢはβO_x（βは金属元素、ｘは金属元素の価数によって決まる酸素の原子数）で表される金属酸化物又は過酸化水素分解酵素であることが好ましい。ここで、本願発明に用いる金属錯体とは、特に断らない限り、単核の金属錯体を指す。単核金属錯体は、先行技術に記載された二核金属錯体に比べ酸化力が弱いので、電池の他の構成要素の酸化劣化を抑制することが可能となる。

【００１０】また、金属錯体の配位子が、窒素原子を有する単座あるいは多座配位子であることが好ましい。さらに好ましくは、配位子が、ポルフィリン環又はフタロシアン環である。また、ポリフィリン環又はフタロシアン環が、重合性の置換基を有することが好ましい。

【００１１】また、金属酸化物には、ペロブスカイト酸化物又はMnO_y（ｙはマンガンの価数によって決まる酸素の原子数）で表されるマンガン酸化物を用いることができる。

【００１２】本発明の酸素還元用電極は、酸素の電気化学還元により過酸化水素を生成する２電子還元反応を触媒する以下の電気化学触媒Ａと、電気化学触媒Ａによる２電子還元反応で生成した過酸化水素を分解して酸素を生成する分解反応を触媒する以下の触媒Ｂと、を少なくとも含有するように構成することができる。

【００１３】また、電気化学触媒Ａと触媒Ｂとが、導電性基材に保持されていることが好ましく、さらに、電気化学触媒Ａが、導電性基材を兼ねることもできる。

【００１４】また、触媒Ｂと、導電性基材及び／又は電気化学触媒Ａとの間を、直接もしくは電子伝導体を介して電子が移動しないように、触媒Ｂを電気的に絶縁することが好ましい。好ましくは、触媒Ｂが、プロトン導電性のポリマーに分散されていることである。

【００１５】電気化学触媒Ａには、金属材料、炭素材料、金属酸化物、そしてαL_n（ｎは配位する配位子の数）で表される中心金属原子αと、該金属原子αに配位する配位子Ｌとを有する金属錯体から成る群から選択された１種を用いることができる。

【００１６】また、金属錯体の配位子には、窒素原子を有する単座あるいは多座配位子を用いることができる。好ましくは、配位子が、ポルフィリン環又はフタロシアニン環を有することである。また、ポリフィリン環又はフタロシアン環は、重合性の置換基を有することもできる。

【００１７】触媒Ｂには、過酸化水素分解酵素又はβO_x（βは金属元素、ｘは金属元素の価数によって決まる酸素の原子数）で表される金属酸化物を用いることができる。

【００１８】また、金属酸化物には、ペロブスカイト酸化物又はMnO_y（ｙはマンガンの価数によって決まる酸素の原子数）で表されるマンガン酸化物を用いることができる。さらに、ペロブスカイト酸化物には、$La_xSr_{1-x}MnO_3$（$x=0〜0.5$）を用いることができる。

【００１９】特に、電気化学触媒ＡがαL_n（ｎは配位する配位子の数）で表される中心金属原子αと、該金属原子αに配位する配位子Ｌとを有する金属錯体であり、触媒Ｂが過酸化水素分解酵素又はβO_x（βは金属元素、ｘは金属元素の価数によって決まる酸素の原子数）で表される金属酸化物であることが好ましい。

【００２０】本発明の酸素還元用複合電極を、酸素の還元反応を正極反応とする、空気電池の正極あるいは燃料電池の正極として用いることにより発電セルを構成することができる。すなわち、本発明は、酸素の電気化学還元により過酸化水素を生成する２電子還元反応を触媒する電気化学触媒Ａと、生成した過酸化水素を分解して酸素を生成する分解反応を触媒する触媒Ｂと、を少なくとも含有する酸素還元用複合電極から成り、上記の複合電極の電極電位は電気化学触媒Ａの酸素還元電位であり、触媒Ｂにより過酸化水素を分解して再生された酸素を電気化学触媒Ａが２電子還元して過酸化水素を繰返し生成する正極と、負極活物質あるいは燃料物質の酸化反応をする負極と、電解質と、を有する発電セルを提供する。

【００２１】上記発電セルは、負極及び電解質の少なくとも一方に、光吸収により励起されて炭水化物を電気化学的に酸化する分子を付与し、該分子に光照射しながら炭水化物を供給して、負極において該分子により炭水化物を酸化せしめて、正極と負極との間に起電力を発生させる、炭水化物を燃料とする発電セルとすることができる。

【００２２】また、上記発電セルにおいて、本発明の酸素還元用複合電極を空気極とし、負極を燃料極とし、空気極と燃料極とがプロトン導電性のイオン交換膜を介して接続させることにより燃料電池を構成することができる。

【００２３】また、上記発電セルにおいて、本発明の酸素還元用複合電極を正極とし、負極に亜鉛、マグネシウム及びアルミニウムから選択されたいずれか１種の金属を用いることにより、亜鉛－空気電池、マグネシウム－空気電池、そしてアルミニウム－空気電池を構成することができる。

【００２４】

【発明の実施の形態】本発明は、酸素を電極反応物質とする酸素還元複合電極を提供する。本発明の酸素還元用複合電極は、酸素の電気化学的還元により過酸化水素を生成する電気化学触媒Ａと、生成した過酸化水素を分解して酸素を生成する触媒Ｂとを少なくとも含有する。電気化学触媒Ａは、$O_2+H_2O+2e^- \rightarrow OH^- + HO_2^-$（アルカリ液中）で表される酸素の２電子還元反応（１）を触媒し、過酸化水素（H_2O_2、アルカリ液中ではHO_2^-で表される過酸化水素イオン）を生成する。

【００２５】触媒Ｂは、生成した過酸化水素イオンを、$2HO_2^- \rightarrow O_2 + 2OH^-$　で表される分解反応（２）を触媒し、酸素が再生される。再生した酸素は、再度、電気化学触媒Ａにより２電子還元を受け、過酸化水素イオンを生成する。酸素１分子が、２電子還元反応（１）により過酸化水素イオン１分子を生成し、生成した過酸化水素イオン１分子は分解反応（２）により1/2分子の酸素を再生する。1/2分子の酸素分子は、２電

子還元反応（１）により1/2分子の過酸化水素イオンを生成し、生成した1/2分子の過酸化イオンは分解反応（２）により1/4分子の酸素を再生する。

【００２６】1/4分子の酸素分子は、２電子還元反応（１）により1/4分子の過酸化水素イオンを生成し、生成した1/4分子の過酸化イオンは分解反応（２）により1/8分子の酸素を再生する。２電子還元反応（１）と分解反応が（２）繰り返し起こり続ける。すなわち、酸素1分子の還元に対して、２電子、１電子、1/2電子、1/4電子、1/8電子、・・・・、（1/2）ｎ　電子（ｎ→無限大）の合計４電子が用いられ、酸素１分子が２電子還元反応の電位で４電子還元反応を受けたのと同じとなり、すなわち、２電子反応であるが、電気量としては２電子反応の２倍の４電子反応（$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$）に相当する反応が起こったことと同じ結果となる。

【００２７】本発明の酸素還元複合電極は、このような酸素の還元経路を与える電気化学触媒Ａと触媒Ｂとを少なくとも含有しているので、酸素の４電子還元を１００％に近い選択率で行うことができる。

【００２８】以下、本発明を詳しく説明する。本発明の電気化学触媒Ａとしては、酸素を電気化学的に還元して過酸化水素（H_2O_2、HO_2^-）を生成するものであれば有機、無機、金属、これらの混合物、複合物、何れの材料も用いることができる。白金、コバルト、ルテニウム、パラジウム、ニッケル、金、銀、銅、白金－コバルト合金、白金－ルテニウム合金などの金属材料、黒鉛や活性炭などの炭素材料、酸化銅、酸化ニッケル、酸化コバルト、酸化ルテニウム、酸化鉛、酸化モリブデン、二酸化マンガン、ルテニウム酸鉛、ランタン－マンガン－銅ペロブスカイト酸化物などの金属酸化物、鉄フタロシアニン、コバルトフタロシアニン、銅フタロシアニン、マンガンフタロシアニン、亜鉛フタロシアニンなどのポルフィリン環を有する金属フタロシアニンあるいは金属ポルフィリン、ルテニウムアンミン錯体、コバルトアンミン錯体、コバルトエチレンジアミン錯体などの金属錯体などを用いることができる。

【００２９】中でも、酸素の電気化学的還元に対して活性の高い、αＬｎで表させる金属錯体が好適に用いられる。金属錯体を用いると、酸素の還元電位を、中心金属元素αの種類あるいは価数を変えるだけでなく配位子Ｌを変えることで貴な（プラス）方向あるいは卑な(マイナス)方向に変えることができるという利点がある。例えば、αが２価のコバルトであるコバルトフタロシアニン錯体（ＰｃＣｏ（ＩＩ）と表す）では、配位子であるフタロシアニン環に電子吸引性のカルボキシル基（－ＣＯＯＨ），シアノ基（－ＣＮ）などを導入することで酸素の２電子還元電位を貴な（プラス）方向に１０から５０ｍＶ変えることができる。

【００３０】また、ＰｃＣｏ（ＩＩ）の他、αが２価の亜鉛である亜鉛フタロシアニン錯体（ＰｃＺｎ（ＩＩ）と表す）やαが２価の銅である銅フタロシアニン錯体（ＰｃＣｕ（ＩＩ）と表す）では、オクタブトキシ基（ＯＢu）などの電子供与性のアルコキシ基をフタロシアニン環に導入することで酸素の２電子還元電位を卑な（マイナス）方向に１０から２００ｍＶ変えることができる。さらに、プロトン解離平衡能を有する配位子から構成される金属錯体では、酸素還元反応を行う際に用いる電解液などの媒体のｐＨを変えることで、酸素の２電子還元電位を数１００ｍＶの間で大きく変化させることができる。

【００３１】配位子（Ｌ）としては、フタロシアニン、オクタブトキシフタロシアニン、オクタシアノフタロシアニン、フタロシアニン４酢酸、テトラ（0－アミノフェニル）ポルフィリン、テトラアミノフタロシアニン、テトラメチルフェニルポルフィリン、テトラフェニルポリフィリン、テトラ（Ｎ－メトキシフェニル）ポリフィリンなどのポルフィリン環を有する配位子、アンモニア、エチレンジアミン、エチレンジアミン４酢酸、４－ビニルピリジン、２－ビニルピリジン、ビピリジルなど、窒素原子（Ｎ）を含有し、この窒素原子を介して中心金属αとで錯体を形成する単座あるいは多座配位子が、比較的安定な金属錯体を形成するので好ましい。なかでも、アミノ基やアミノフェニル基などの重合性の置換基を有するテトラアミノフタロシアニンやテトラ（0－アミノフェニル）ポリフィリンなどの配位子は、重合により高分子化したさらに安定性が増した金属錯体を形成することができるので好ましい。

【００３２】次に、このような金属錯体（αＬｎ）の中心金属元素（α）としては、白金、ルテニウム、コバルト、マンガン、鉄、銅、銀、亜鉛などが、酸素の還元反応をより小さな過電圧で進行できるので好ましい。また、αの価数は４以下が好ましい。価数を４以下とすることで、触媒の酸化力を抑え、金属錯体と一緒に用いられる電池や他の構成要素、例えば、電解液、電極リード、集電体、電池ケース、セパレータ、ガス選択透過膜などの酸化劣化を有効に防止することができる。

【００３３】本発明の触媒Ｂとしては、過酸化水素を分解して酸素を生成する有機、無機、金属、これらの混合物、複合物、何れの材料も用いることができる。また、カタラーゼなどの過酸化水素分解酵素などを有効に用いることができる。なかでも、過酸化水素と親和性が高く、酸素を取り込んだり放出したりする酸素交換能力の高いβO_xで表される金属酸化物が好ましい。このような金属酸化物として、$MnSO_4$などの２価のマンガン塩を過酸化水素などで化学酸化し、必要に応じさらに酸素ガスを含む雰囲気中で加熱酸化することで得られるMn_2O_3，Mn_3O_4、Mn_5O_8、γ－ＭｎＯＯＨ（Mn_3O_4とMn_5O_8の混合物）などのマンガン酸化物（MnO_y）、白金黒、酸化ルテニウム、Ｃｕ

$_{x-1}$ Sr_xTiO_3（x＝０～０．５）、$La_xSr_{1-x}MnO_3$（x＝０～０．５）、$SrTiO_3$ などのペロブスカイト酸化物などがある。なかでも、マンガン低級酸化物は過酸化水素の分解活性が高く、劣化が少なく、しかも安価であるので好ましい。マンガン低級酸化物とは、マンガン原子の原子価が４に満たないマンガン酸化物のことで、使用後のマンガン乾電池の二酸化マンガン正極をそのまま、あるいは焼成したものを用いることができるので、資源再利用の観点からも特に好ましい。

【００３４】本発明の酸素還元用複合電極は、電気化学触媒Ａと触媒Ｂとを保持する導電性基材を有している。導電性基材は、金属材料、炭素質材料、導電性酸化物材料等からなり、板状、棒状、円筒状、ディスク状、あるいは多孔体等の種々の形状のものを用いることができ、集電体を兼ねることもできる。

【００３５】なお、電気化学触媒Ａは導電性基材を兼ねることもできる。この場合、触媒Ｂを電気化学触媒Ａの表面に保持させる必要がある。

【００３６】本発明の酸素還元用複合電極内にあって電気化学触媒Ａと触媒Ｂは、お互いに接して配置してもあるいは離れて配置してもよいが、お互いに相手の近傍に配置するのが好ましい。こうすることで、電気化学触媒Ａにおいて酸素の電気化学的還元により生成した過酸化水素は、移動過程を経ずあるいは最短距離の移動を経て触媒Ｂに至り分解し酸素を再生し、再生した酸素は、やはり移動過程を経ずあるいは最短距離の移動を経て電気化学触媒Ａに至って還元を受けることができる。酸素還元用複合電極全体として酸素還元の過電圧を小さくすることができる。さらに、電気化学触媒Ａとして金属錯体を用いると、金属錯体は分子一つ一つが酸化還元能力を有しているので、電気化学触媒Ａと触媒Ｂは分子オーダーで近接することが可能で、より小さな過電圧の酸素還元用複合電極が得られる。

【００３７】酸素の電気化学的還元に必要な電子を、酸素還元用複合電極と組合せて用いる電気化学的酸化反応を行う電極から供給をうけるために、電気化学触媒Ａは、導電性基材上に保持され、電極リード及び／又は接続導体に電気的に接続される。

【００３８】一方、触媒Ｂは、導電性基材上に保持されている必要は必ずしもない。むしろ、これらから電気的に絶縁した状態で配置されるのが望ましい。触媒Ｂを電気的に絶縁した状態で配置することで、過酸化水素を分解して酸素を生成する作用ならびに酸素の電解還元を行う作用の両方を有する材料も触媒Ｂとして用いることが可能となる。この場合、触媒Ｂは電気的に絶縁した状態で配置されるので電気化学反応は起こらず、酸素を生成する過酸化水素の分解のみを起こすことができる。

【００３９】したがって、本発明の酸素還元用複合電極の電極電位は、電気化学触媒Ａの酸素還元電位によってのみ決定され、前記電極を用いた電気化学デバイスの設計が容易となる。また、触媒Ｂとしては、先に示した材料の他、酸素の還元反応と過酸化水素の分解反応の両方に活性な材料であっても用いることができる。このような材料として、白金、金、ルテニウム、パラジウム、二酸化マンガン、活性炭、黒鉛、金属ポルフィリン化合物、金属フタロシアニン化合物がある。さらに、酸素の還元反応以外の余分な電気化学反応が起こらないので、生成した過酸化水素が余分な電気化学反応で生成した被還元種と反応して消費されたり、再生した酸素が余分な電気化学反応で生成した被酸化種と反応して消費されたりすることを有効に防止することができ、見かけ上１００％に近い選択率で酸素の４電子還元反応が可能となる。

【００４０】酸素を還元して過酸化水素を生成する電気化学触媒Ａであれば、過酸化水素を分解して酸素を生成するいずれの触媒Ｂとも複合化して用いることに制限はない。但し、本発明の酸素還元用複合電極を正極として用い、正極に電子を外部回路を通して供給する負極と組合せて、空気電池や燃料電池などの発電セルを構成する際、負極に用いる電極活物質あるいは燃料物質が電解質に溶解し正極と接触する虞がある場合は、酸素還元反応の選択性の高い電気化学触媒Ａと過酸化水素の分解の選択性の高い触媒Ｂの組合せを好適に選択することができる。電解質に溶解するメタノール、エタノール、エチレングリコール、グルコースなどの糖類を燃料とする燃料電池では、電気化学触媒Ａには酸素還元反応の選択性の高い金属フタロシアニン錯体、金属ポリフィリン錯体を選び、触媒Ｂとしては、酸化力が低く過酸化水素分解能の高いMn_2O_3やMn_5O_8などのマンガン低級酸化物あるいは過酸化水素の分解に対して高い選択性を有するカタラーゼなどの酵素を選び、複合化して本発明の酸素還元用複合電極として用いるのが好ましい。

【００４１】本発明の酸素還元用複合電極を作製するため、電気化学触媒Ａと触媒Ｂを導電性基材に保持させるには、触媒を含む塗液を塗布する塗布法や、電気化学的堆積法等の湿式法、又は真空蒸着法等の乾式法、あるいは、バインダーを用いてシート状にした触媒層を導電性基材に圧着する方法等を用いることができる。例えば、塗布法の場合、電気化学触媒Ａを含む塗液を導電性基材の表面に塗布して第１の触媒層を形成し、その第１の触媒層の上に触媒Ｂを含む塗液を塗布して第２の触媒層を形成することが好ましい。触媒Ｂが導電性基材に直接、接触するのを防止するためである。

【００４２】また、第２の触媒層を形成するに際し、触媒Ｂを含む塗液にプロトン導電性のポリマー、例えば、パーフルオロスルホン酸ポリマーを含有させることが好ましい。第２の触媒層にプロトン導電性のポリマーを含有させることにより、過酸化水素の分解反応により生成する水酸化物イオンが速やかに、プロトンと反応して除

去されるので、過酸化水素の分解反応をより促進させることが可能となる。

【００４３】また、触媒自身が、電解析出あるいは電解重合が可能であれば、定電位又は定電流、あるいは電位スイープ等の方法により導電性基材上に堆積させて、触媒層を形成することができる。例えば、電気化学触媒Ａに前記の、アミノ基やアミノフェニル基等の重合性の置換基を有するテトラアミノフタロシアニンやテトラ（0ーアミノフェニル）ポルフィリン等の配位子を有する金属錯体を用いると、電解重合によりアミノ基を介して高分子化した金属錯体から成る触媒層を形成することができる。この高分子化した金属錯体から成る触媒層の上に、塗布法あるいは電気化学堆積法等により触媒Ｂを含む触媒層を形成することができる。

【００４４】本発明の酸素還元用複合電極と組み合わせて用いる電解液としては、水溶液、有機電解液いずれの電解液でも用いることができる。O_2 の溶解度が大きくかつ拡散速度の速い１Ｍ以下の低濃度のアルカリ性の水溶液は、電解反応を効率よく起こすことができるので特に好ましい。以下、本発明を、実施例によって具体的に説明する。

【００４５】

【実施例】（実施例１）

（１）試験電極１１、１２、１３、１４、１５の作製

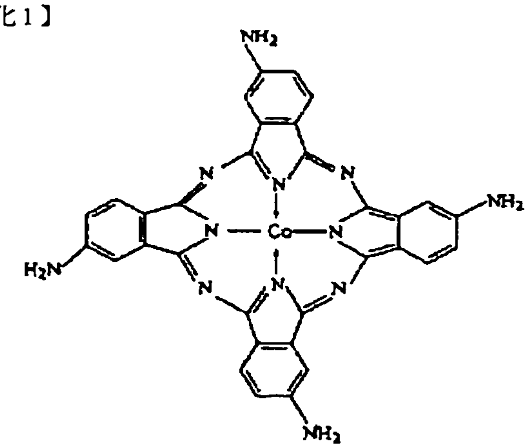
電気化学触媒Ａとしてポリーコバルトー４，４’，４”，４’”ーテトラアミノフタロシアニン（p-CoTAPc）、触媒Ｂとしてγ－ＭｎＯＯＨ（Mn_3O_4 とＭｎ$_5O_8$ との混合物）を用いて、直径６mmのグラッシーカーボン（ＧＣ）を用いて試験電極を作製した。グラッシーカーボンは、厚さ５mm、直径６mmのペレットであり、一方の面を電極リード線と接続し、もう一方の面が露出した状態で、直径１０mm、長さ８０mmのポリイミド樹脂製の鞘に埋め込んだ。露出した面上に何も形成していない状態のＧＣを、試験電極１３とした。

【００４６】０．１Ｍのりん酸テトラブチルアンモニウムを溶解したジメチルスフホキシド（ＤＭＳＯ）溶液に、化１に示した構造式を有するコバルトー４，４’，４”，４’”ーテトラアミノフタロシアニン（CoTAPc）を、０．２mM溶解することで、電解液を作成した。この電解液中で、ＧＣを作用極、白金を対極、Ａｇ／ＡｇＣｌ（飽和ＫＣｌ）電極を参照電極として電解を行い、ＧＣの露出した面上に、p-CoTAPcを形成した。

【００４７】電解は、ＧＣの電位をＡｇ／ＡｇＣｌ参照電極に対し、プラス０．５Ｖからマイナス１．４Ｖの間で、５０ｍＶ／ｓの速度で増減を３０回繰り返し行うことで、p-CoTAPcをＧＣの上に形成した。これを電極１２とした。ここで、ｐ-CoTAPcは、 CoTAPcの４，４’，４”，４”’位のアミノ基が電解酸化を受けこのアミノ基を介して高分子化したものである。

【００４８】

【化１】



【００４９】次に、プロトン伝導性のパーフルオロスルホン酸ポリマー（デュポン社製：Ｎａｆｉｏｎ１１２）を０．０５重量％溶解したエタノール溶液５μｌに、γ－ＭｎＯＯＨ粉末を２５μｇ分散し、これを前述のp-CoTAPcを形成したＧＣの全面を覆うように滴下した。つぎに、これを温風乾燥してエタノールを蒸発させ、さらに同溶液を５μｌ滴下し、エタノールを蒸発させることで、試験電極１１を作製した。

【００５０】次に、γ－ＭｎＯＯＨを分散させた上記のエタノール溶液を５μｌ、裸のＧＣの全面を覆うように滴下し、エタノールを蒸発させる操作を２回繰返して、試験電極１４を作製した。

【００５１】次に、γ－ＭｎＯＯＨを分散させた上記のエタノール溶液を５μｌ、裸の金（Ａｕ）電極の全面を覆うように滴下し、エタノールを蒸発させる操作を２回繰返して、試験電極１５を作製した。ここで用いたＡｕ電極は、長さ５ｍｍ、直径６ｍｍのペレットであり、一方の面を電極リード線と接続し、他方の面を露出させた状態で、直径１０ｍｍ、長さ８０ｍｍのポリイミド製の鞘の中に埋め込んで作製したものである。

【００５２】（２）試験電極の酸素還元特性の評価

以上の工程により作製した試験電極を、作用電極、白金を対極、Ａｇ／ＡｇＣｌ（飽和ＫＣｌ）電極を参照電極とする３極セルを構成して、酸素の還元特性を評価した。電解液には、ｐＨ７．４の０．１Ｍりん酸緩衝溶液を用いた。酸素ガスを３０分間電解液中に通じて溶存酸素を飽和したのち電解を行った。作用電極の電位を、参照電極に対して＋０．１Ｖから－１．２Ｖに５０ｍＶ／ｓの速度で減少し、－１．２Ｖに達すると、０Ｖに向かって５０ｍＶ／ｓの速度で増加し、この際、作用電極と対極の間を流れる電解電流を、作用電極の電位に対して記録した。

【００５３】図１は、試験電極１１、１２、１３について得られた電流－電位曲線である。図１において、酸素の還元反応に対応する還元電流のピーク電位（Ｅｐ）は、試験電極１１では、－０．４５Ｖ、試験電極１２では、－０．３５Ｖ、試験電極１３では、－０．７５Ｖで

あった。

【００５４】p-CoTAPcをＧＣ上に形成することで、酸素の還元電位は、－０．７５Ｖから－０．３５～－０．４５Ｖにプラス側にシフトし、より貴な電位で酸素の還元が行える。p-ＣoTAPc（電気化学触媒Ａ）とＭｎＯＯＨ（触媒Ｂ）とを複合化した本発明の試験電極１１は、p-CoTAPcのみの試験電極１２に較べ、ほぼ２倍の酸素還元ピーク電流値を得た。これは、p-CoTAPcの作用により、酸素の２電子還元により生成した過酸化水素が、ＭｎＯＯＨの作用により分解して酸素を再生し、再生した酸素がp-CoTAPcにより還元される反応サイクルが繰り返し起こり、酸素の４電子還元に相当するため、２倍のピーク電流値が得らたものと考える。すなわち、本発明に従う試験電極１１では、より貴な電位で電子還元をほぼ１００％に近い選択率で行うことができた。

【００５５】図２は、試験電極１１，１２，１３のそれぞれについて、それぞれのピーク電位（Ｅｐ）で定電位電解を連続的に行った際の、電流－時間曲線を示したである。いずれの試験電極でも、電解開始後３０秒程で電流はほぼ一定の定常電流値（Ｉst）に達する。定常電流値は、比較例の試験電極１２および１３では、１２～１３μＡ、本発明に従う試験電極１１では、２５μＡである。試験電極１１では、試験電極１２あるいは１３に較べ約２倍の定常電流値を与え、酸素が見かけ上４電子反応でほぼ１００％に近い選択率で還元されている。

【００５６】試験電極１１，１２，１３，１４，１５のそれぞれについて、Ｅｐ値、定電位電解２００秒後のＩst値、１２０時間後のＩst値を、表１にまとめて示した。

【００５７】なお、定電位電解は酸素ガスを電解液に吹き込みながら行った。

【００５８】

【表１】

試験電極	電気化学触媒Ａ	触媒Ｂ	酸素還元電流のピーク電位 Ep(V) vs. Ag/AgCl	ピーク電位での定電位電解時の定常電流値　Ist. (μA)	
				電解 200 秒後	電解 120 時間後
１１	p-CoTAPc	MnOOH	−0.45	25	23
１２	p-CoTAPc	…	−0.35	13	12
１３	GC	…	−0.75	13	…
１４	GC	MnOOH	−0.75	18	…
１５	Au	MnOOH	−0.35	24	…
２１	CoTAPc	MnOOH	−0.40	26	15
２２	CoTAPc	…	−0.35	12	6
３１	CoHFPc	MnOOH	−0.20	15	…
３２	CoHFPc	…	−0.15	8	…
４１	CoCOOHPc	MnOOH	−0.15	20	…
４２	CoCOOHPc	…	−0.05	11	…
５１	CoOBuPc	MnOOH	−0.35	28	…
５２	CoOBuPc	…	−0.25	16	…
６１	p-CoTAPc	カタラーゼ	−0.35	29	…
６２	CoHFPc	カタラーゼ	−0.15	18	…
６３	CoCOOHPc	カタラーゼ	−0.05	22	…
６４	CoOBuPc	カタラーゼ	−0.26	30	…
６５	GC	カタラーゼ	−0.75	22	…
６６	Au	カタラーゼ	−0.35	26	…
７１	p-CoTAPc	$La_{0.8}Sr_{0.2}MnO_3$	−0.40	27	…
７２	CoHFPc	$La_{0.8}Sr_{0.2}MnO_3$	−0.15	16	…
７３	CoCOOHPc	$La_{0.8}Sr_{0.2}MnO_3$	−0.10	20	…
７４	CoOBuPc	$La_{0.8}Sr_{0.2}MnO_3$	−0.25	28	…
７５	GC	$La_{0.8}Sr_{0.2}MnO_3$	−0.75	21	…
７６	Au	$La_{0.8}Sr_{0.2}MnO_3$	−0.35	25	…

【００５９】（実施例２）

（３）試験電極２１、２２の作製

電気化学触媒Ａとして、コバルト－テトラアミノフタロシアニン（CoTAPc）、触媒Ｂとしてγ－ＭｎＯＯＨ（Mn_3O_4 と Mn_5O_8 との混合物）を用いて試験電極を、実施例１と同様の直径６ｍｍのＧＣを用いて作製した。

【００６０】１ｍＭのCoTAPcをN,N'-ジメチルホルムアミド（ＤＭＦ）に溶解した溶液５μｌを、ＧＣの露出した面を覆い尽くすように滴下したのち、２時間温風乾燥することでCoTAPcを表面に有する試験電極２２を作成した。 次に、γ－ＭｎＯＯＨ粉末を２５μｇ分散し、かつナフィオンを０．０５重量％溶解したエタノール溶液５μｌをCoTAPcを有するＧＣの全面を覆うように滴下し、温風乾燥してエタノールを蒸発させ、さらに同溶液を５μｌ滴下しエタノールを蒸発させ、CoTAPcとＭｎＯＯＨを表面に有する本発明に従う試験電極２１を作製した。

【００６１】（４）試験電極の酸素還元特性の評価

以上の工程により作製した試験電極を、作用電極、白金を対極、Ａｇ／ＡｇＣｌ（飽和ＫＣｌ）電極を参照電極とする３極セルを構成して、酸素の還元特性を評価し

た。電解液には、ｐＨ７．４の０．１Ｍりん酸緩衝溶液を用いた。酸素ガスを３０分間電解液中に通じて溶存酸素を飽和したのち電解を行った。作用電極の電位を、参照電極に対して＋０．１Ｖから－１．２Ｖに５０ｍＶ／ｓの速度で減少し、－１．２Ｖに達すると、０Ｖに向かって５０ｍＶ／ｓの速度で増加し、この際、作用電極と対極の間を流れる電解電流を、作用電極の電位に対して記録した。

【００６２】CoTAPc（電気化学触媒Ａ）とＭｎＯＯＨ（触媒Ｂ）とを複合化した本発明の試験電極２１は、CoTAPcのみの試験電極２２に較べ、ほぼ２倍の酸素還元ピーク電流値を与えた。酸素の還元反応に対応する還元電流のピーク電位（Ｅｐ）を表１に示した。試験電極２１では－０．４０Ｖ、試験電極２２では、－０．３５Ｖである。酸素の還元電位は、－０．７５Ｖから－０．４０～－０．３５Ｖにプラス側にシフトし、より貴な電位で酸素の還元が行える。

【００６３】次に、試験電極２１、２２のそれぞれについて、それぞれのピーク電位（Ｅｐ）で定電位電解を連続的に行った。定電位電解後のＩst値を表１に示す。定常電流値は、比較例の試験電極２２では、１２μＡ（２００秒後）、６μＡ（１２０時間後）であるのに対し、本発明に従う試験電極２１では、２６μＡ（２００秒後）、１５μＡ（１２０時間後）である。試験電極２１では、試験電極２２に較べ約２倍の定常電流値を与え、酸素が４電子反応でほぼ１００％に近い選択率で還元されている。

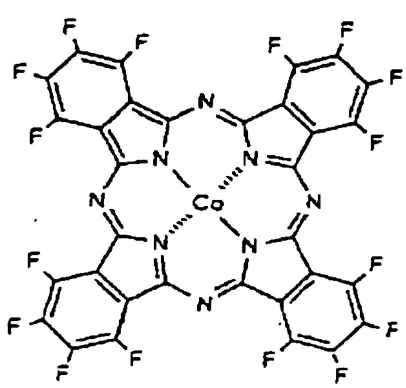
【００６４】（実施例３）

（５）試験電極３１、３２の作製

電気化学触媒Ａとして、化２に示した構造式を有するコバルト－ヘキサデカフルオロフタロシアニン（CoHFPc）、触媒Ｂとしてγ－ＭｎＯＯＨ（Mn_3O_4 と Mn_5O_8 との混合物）を用いて試験電極を、実施例１と同様の直径６ｍｍのＧＣを用いて作製した。

【００６５】

【化２】



【００６６】１ｍMのCoHFPcをＤＭＦに溶解したＤＭＦ溶液５μｌを、ＧＣの露出した面を覆い尽くすように滴下したのち、２時間温風乾燥し、さらに、同じＤＭＦ溶液５μｌを滴下して、２時間温風乾燥することで、CoHFPcを表面に有する試験電極３２を作製した。

【００６７】一方、５０μｇのγ－ＭｎＯＯＨ粉末を前記ＤＭＦ溶液に分散した溶液５μｌをＧＣの露出した面を覆い尽くすように一度だけ滴下したのち、２時間温風乾燥した。さらに、前記ＤＭＦ溶液を、CoHFPcを有するＧＣの全面を覆うように滴下し、温風乾燥してＤＭＦを蒸発させることで、CoHFPcとＭｎＯＯＨとを表面にする本発明に従う試験電極３１を作製した。

【００６８】（６）試験電極の酸素還元特性の評価

以上の工程により作製した試験電極を、作用電極、白金を対極、Ａｇ／ＡｇＣｌ（飽和ＫＣｌ）電極を参照電極とする３極セルを構成して、酸素の還元特性を評価した。電解液には、ｐＨ７．４の０．１Ｍりん酸緩衝溶液を用いた。純酸素ガスを３０分間電解液中に通じて溶存酸素を飽和したのち電解を行った。作用電極の電位を、参照電極に対して＋０．１Ｖから－１．２Ｖに５０ｍＶ／ｓの速度で減少し、－１．２Ｖに達すると、０Ｖに向かって５０ｍＶ／ｓの速度で増加し、この際、作用電極と対極の間を流れる電解電流を、作用電極の電位に対して記録した。

【００６９】CoHFPc（電気化学触媒Ａ）とＭｎＯＯＨ（触媒Ｂ）とを複合化した本発明に従う試験電極３１では、CoHFPcのみの試験電極３２に較べ、ほぼ２倍の酸素還元ピーク電流値を与えた。酸素の還元反応に対応する還元電流のピーク電位（Ｅｐ）を表１に示す。試験電極３１では－０．２０Ｖ、試験電極２２では、－０．１５Ｖである。酸素の還元電位は、－０．７５Ｖから－０．１５～－０．２０Ｖにプラス側にシフトし、より貴な電位で酸素の還元が行える。

【００７０】次に、試験電極３１，３２のそれぞれについて、それぞれのピーク電位（Ｅｐ）で定電位電解を連続的に行った。定電位電解２００秒後のＩst値を表１に示す。定常電流値は、比較例の試験電極２２では、８μＡであるのに対し、本発明に従う試験電極３１では、１５μＡである。試験電極３１では、試験電極３２に較べ約２倍の定常電流値を与え、酸素が見かけ上４電子反応でほぼ１００％に近い選択率で還元されている。

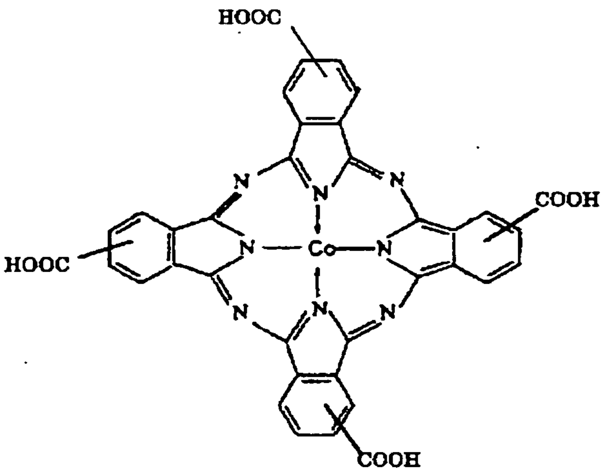
【００７１】（実施例４）

（７）試験電極４１、４２の作製

電気化学触媒Ａとして、化３に構造式を示したコバルト－テトラカルボキシフタロシアニン（CoCOOHPc）、触媒Ｂとしてγ－ＭｎＯＯＨ（Mn_3O_4 と Mn_5O_8 との混合物）を用いて試験電極を、実施例１と同様の直径６ｍｍのＧＣを用いて作製した。

【００７２】

【化３】



【００７３】１ｍMのCoCOOHPcをＤＭＦに溶解したＤＭＦ溶液５μｌをＧＣの露出した面を覆い尽くすように滴下したのち、２時間温風乾燥し、さらに、同じＤＭＦ溶液５μｌを滴下して２時間温風乾燥することで、CoCOOHPcを表面に有する試験電極４２を作製した。

【００７４】一方、５０μｇのγ－ＭｎＯＯＨ粉末を前記ＤＭＦ溶液に分散した溶液５μｌを、前記ＤＭＦ溶液５μｌを一度だけ滴下して２時間温風乾燥することで作成したCoCOOHPcを有するＧＣの全面を覆うように滴下し、温風乾燥してＤＭＦを蒸発させCoCOOHPcとＭｎＯＯＨを表面に有する本発明に従う試験電極４１を作製した。

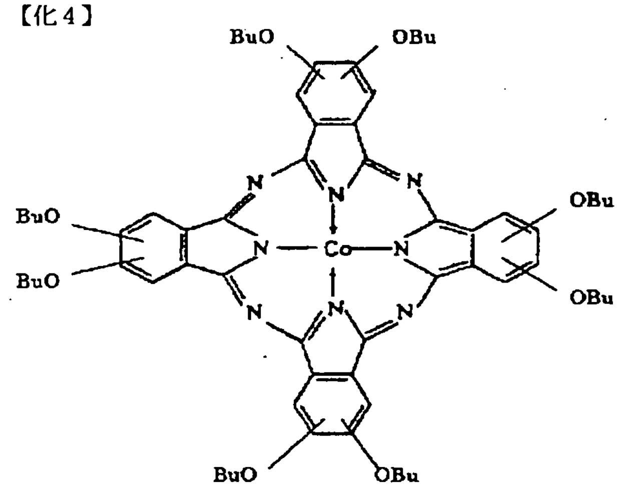
【００７５】（８）試験電極の酸素還元特性の評価
以上の工程により作製した試験電極を作用電極、白金を対極、Ａｇ／ＡｇＣｌ（飽和ＫＣｌ）電極を参照電極とする３極セルを構成して、酸素の還元特性を評価した。電解液には、ｐＨ７．４の０．１Ｍりん酸緩衝溶液を用いた。酸素ガスを３０分間電解液中に通じて溶存酸素を飽和したのち電解を行った。作用電極の電位を、参照電極に対して＋０．１Ｖから－１．２Ｖに５０ｍＶ／ｓの速度で減少し、－１．２Ｖに達すると、０Ｖに向かって５０ｍＶ／ｓの速度で増加し、この際、作用電極と対極の間を流れる電解電流を、作用電極の電位に対して記録した。

【００７６】ＣoCOOHPc（電気化学触媒Ａ）とＭｎＯＯＨ（触媒Ｂ）とを複合化した本発明に従う試験電極４１では、CoCOOHPcのみの試験電極４２に較べ、ほぼ２倍の酸素還元ピーク電流値を与えた。酸素の還元反応に対応する還元電流のピーク電位（Ｅｐ）を表１に示す。試験電極４１では－０．１５Ｖ、試験電極４２では、－０．０５Ｖである。酸素の還元電位は、－０．７５Ｖから－０．０５～－０．１５Ｖにプラス側にシフトし、より貴な電位で酸素の還元が行える。

【００７７】次に、試験電極４１，４２のそれぞれについて、それぞれのピーク電位（Ｅｐ）で定電位電解を連続的に行った。定電位電解２００秒後のＩst値を表１に示す。定常電流値は、比較例の試験電極４２では、１１μＡであるのに対し、本発明に従う試験電極４１では、２０μＡである。試験電極４１では、試験電極４２に較べ約２倍の定常電流値を与え、酸素が見かけ上４電子反応でほぼ１００％に近い選択率で還元された。

【００７８】（実施例５）
（９）試験電極５１、５２の作製
電気化学触媒Ａとして、化４に構造式を示したコバルト－オクタブトキシフタロシアニン（CoOBuPc）、触媒Ｂとしてγ－ＭｎＯＯＨ（Mn_3O_4とMn_5O_8との混合物）を用いて試験電極を、実施例１と同様の直径６ｍｍのＧＣを用いて作製した。

【００７９】
【化４】



【００８０】１ｍMのCoOBuHPcを、酸素透過性のポリー４－ビニルピリジンを０．０５重量％溶解したＤＭＦに溶解した。このＤＭＦ溶液５μｌをＧＣの露出した面を覆い尽くすように滴下したのち、２時間温風乾燥し、さらに、同じDMF溶液５μｌを滴下して２時間温風乾燥することで、CoOBuPcを表面に有する試験電極５２を作成した。一方、γ－ＭｎＯＯＨ粉末５０μｇを前記ＤＭＦ溶液に分散した溶液５μｌを、ＧＣが露出した面を覆い尽くすように滴下したのち、２時間温風乾燥した。さらに同じ溶液５μｌを滴下、温風乾燥してＤＭＦを蒸発させることで、CoOBuPcとＭｎＯＯＨを表面に有する本発明に従う試験電極５１を作製した。

【００８１】（１０）試験電極の酸素還元特性の評価
以上の工程により作製した試験電極を作用電極、白金を対極、Ａｇ／ＡｇＣｌ（飽和ＫＣｌ）電極を参照電極とする３極セルを構成して、酸素の還元特性を評価した。電解液には、ｐＨ７．４の０．１Ｍりん酸緩衝溶液を用いた。純酸素ガスを３０分間電解液中に通じて溶存酸素を飽和したのち電解を行った。作用電極の電位を、参照電極に対して＋０．１Ｖから－１．２Ｖに５０ｍＶ／ｓの速度で減少し、－１．２Ｖに達すると、０Ｖに向かって５０ｍＶ／ｓの速度で増加し、この際、作用電極と対

極の間を流れる電解電流を、作用電極の電位に対して記録した。

【００８２】CoOBuPc（電気化学触媒Ａ）とＭｎＯＯＨ（触媒Ｂ）とを複合化した本発明に従う試験電極５１では、CoCOOHPcのみの試験電極５２に較べ、ほぼ２倍の酸素還元ピーク電流値を与えた。酸素の還元反応に対応する還元電流のピーク電位（Ｅｐ）を表１に示す。試験電極５１では－０．３５Ｖ、試験電極５２では、－０．２５Ｖである。酸素の還元電位は、－０．７５Ｖから－０．３５～－０．２５Ｖにプラス側にシフトし、より貴な電位で酸素の還元が行える。

【００８３】次に、試験電極５１，５２のそれぞれについて、それぞれのピーク電位（Ｅｐ）で定電位電解を連続的に行った。定電位電解２００秒後のＩst値を表１に示す。定常電流値は、比較例の試験電極５２では、１６μＡであるのに対し、本発明に従う試験電極５１では、２８μＡである。試験電極５１では、試験電極５２に較べ約２倍の定常電流値を与え、酸素が見かけ上、４電子反応でほぼ１００％に近い選択率で還元された。

【００８４】（実施例６）

（１１）試験電極６１、６２、６３、６４、６５、６６の作製

電気化学触媒Ａとして、p-CoTAPc、CoHFPc、CoCOOHPc、CoOBuPc、触媒Ｂとして過酸化水素分解酵素であるカタラーゼを用いて試験電極を、実施例１と同様の直径６ｍｍのＧＣを用いて作製した。

【００８５】試験電極２１、３１、４１、５１に触媒Ｂとして用いたＭｎＯＯＨに代えて、カタラーゼを用いた以外は、試験電極２１、３１、４１、５１の作製方法と同じ方法で試験電極６１、６２、６３、６４を作製した。

【００８６】また、試験電極１４の触媒Ｂとして用いたＭｎＯＯＨに代えてカタラーゼを用いた以外は、試験電極１４の作製方法と同じ方法で試験電極６５を作製した。

【００８７】また、試験電極１５の触媒Ｂとして用いたＭｎＯＯＨに代えてカタラーゼを用いた以外は、試験電極１５の作製方法と同じ方法で試験電極６６を作製した。

【００８８】（１２）試験電極の酸素還元特性の評価

以上の工程で作製した試験電極を作用電極、白金を対極、Ａｇ／ＡｇＣｌ（飽和ＫＣｌ）電極を参照電極とする３極セルを構成して、酸素の還元特性を評価した。電解液には、ｐＨ７．４の０．１Ｍりん酸緩衝溶液を用いた。酸素ガスを３０分間電解液中に通じて、溶存酸素を飽和したのち電解を行った。作用電極の電位を、参照電極に対して＋０．１Ｖから－１．２Ｖに５０ｍＶ／ｓの速度で減少し、－１．２Ｖに達すると、０Ｖに向かって５０ｍＶ／ｓの速度で増加し、この際、作用電極と対極の間を流れる電解電流を、作用電極の電位に対して記録した。

【００８９】電気化学触媒Ａと触媒Ｂとを複合化した本発明に従う試験電極６１、６２、６３、６４では、触媒Ｂを含まない試験電極２２、３２、４２、５２に較べ、ほぼ２倍の酸素還元ピーク電流値を与えた。酸素の還元反応に対応する還元電流のピーク電位（Ｅｐ）を表１に示す。　酸素の還元電位は、－０．７５Ｖから－０．３５～－０．０５Ｖにプラス側にシフトし、より貴な電位で酸素の還元が行える。

【００９０】次に、試験電極６１、６２、６３、６４、６５、６６のそれぞれについて、それぞれのピーク電位（Ｅｐ）で定電位電解を連続的に行った。定電位電解２００秒後のＩst値を表１に示す。定常電流値は、本発明に従う試験電極６１、６２、６３、６４、６５、６６では、１８～３０μＡである。触媒Ｂを含まない試験電極２２、３２、４２、５２に較べ約２倍の定常電流値を与え、酸素が見かけ上、４電子反応でほぼ１００％に近い選択率で還元された。

【００９１】（実施例７）

（１３）試験電極７１、７２、７３、７４、７５、７６の作製

電気化学触媒Ａとして、p-CoTAPc、CoHFPc、CoCOOHPc、CoOBuPc、触媒Ｂとしてペロブスカイト酸化物$La_{0.8}Sr_{0.2}MnO_3$を用いて試験電極を、実施例１と同様の直径６ｍｍのＧＣを用いて作製した。

【００９２】試験電極２１、３１、４１、５１に触媒Ｂとして用いたＭｎＯＯＨに代えて、$La_{0.8}Sr_{0.2}MnO_3$を用いた以外は、試験電極２１、３１、４１、５１の作製方法と同じ方法で試験電極７１、７２、７３、７４を作製した。

【００９３】また、試験電極１４に触媒Ｂとして用いたＭｎＯＯＨに代えて、$La_{0.8}Sr_{0.2}MnO_3$を用いた以外は、試験電極１４の作製方法と同じ方法で試験電極７５を作製した。

【００９４】また、試験電極１５に触媒Ｂとして用いたＭｎＯＯＨに代えて、$La_{0.8}Sr_{0.2}MnO_3$を用いた以外は、試験電極１５の作製方法と同じ方法で試験電極７６を作製した。

【００９５】（１４）試験電極の酸素還元特性の評価

上記工程により作製した試験電極を作用電極、白金を対極、Ａｇ／ＡｇＣｌ（飽和ＫＣｌ）電極を参照電極とする３極セルを構成して、酸素の還元特性を評価した。電解液には、ｐＨ７．４の０．１Ｍりん酸緩衝溶液を用いた。酸素ガスを３０分間電解液中に通じて溶存酸素を飽和したのち電解を行った。作用電極の電位を、参照電極に対して＋０．１Ｖから－１．２Ｖに５０ｍＶ／ｓの速度で減少し、－１．２Ｖに達すると、０Ｖに向かって５０ｍＶ／ｓの速度で増加し、この際、作用電極と対極の間を流れる電解電流を、作用電極の電位に対して記録した。

【００９６】電気化学触媒Ａと触媒Ｂとを複合化した本発明に従う試験電極７１、７２、７３、７４、７５、７６では、触媒Ｂを含まない試験電極２２、３２、４２、５２に較べ、ほぼ２倍の酸素還元ピーク電流値を与えた。酸素の還元反応に対応する還元電流のピーク電位（Ｅｐ）を表１に示す。酸素の還元電位は、－０．７５Ｖから－０．４０～－０．１０Ｖにプラス側にシフトし、より貴な電位で酸素の還元が行える。

【００９７】次に、試験電極７１、７２、７３、７４、７５、７６のそれぞれについて、それぞれのピーク電位（Ｅｐ）で定電位電解を連続的に行った。定電位電解２００秒後のＩst値を表１に示す。定常電流値は、本発明に従う試験電極７１、７２、７３、７４、７５、７６では、１６～２８μＡである。触媒Ｂを含まない試験電極２２、３２、４２、５２に較べ約２倍の定常電流値を与え、酸素が見かけ上、４電子反応でほぼ１００％に近い選択率で還元された。

【００９８】なお、中心金属のコバルト（Ｃｏ）を鉄（Ｆｅ）、マンガン（Ｍｎ）に全部あるいは一部置き換えて試験電極７１から７４に相当する試験電極を作製し、酸素還元特性を評価したところ、中心金属がコバルト（Ｃｏ）の金属錯体を用いた試験電極とほぼ同様の効果、すなわち、酸素の還元電位が貴（プラス）な方向にシフトし、約２倍のピーク電流値ならびに定常電流値を得た。

【００９９】（実施例８）

（１３）発電セルの組み立て

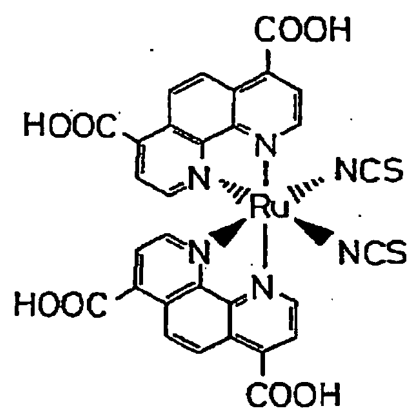
図３に示す構成の発電セルＡおよび発電セルＢを組み立てた。

【０１００】正極として作用する空気極（６）は、発電セルＡでは、化３に構造式を示したコバルトテトラカルボキシフタロシアニン（CoCOOHPc）を２．０重量％添着したMn_2O_3粉末２重量部、活性炭粉末１重量部、アセチレンブラック粉末０．３重量部、ポリテトラフルオロエチレン（ＰＴＦＥ）バインダー０．２重量部からなる混合物を、厚さ０．２ｍｍのニッケルスクリーンに埋め込み保持させて作製した。

【０１０１】負極として作用する光触媒電極は、ガラス基板（１）、ＩＴＯ薄膜（２）、TiO_2微粒子膜（３）、および色素分子で構成した。厚さ１ｍｍのガラス基板（１）上に表面抵抗が１０オーム／□のインジウム・錫酸化物（ＩＴＯ）薄膜（２）が形成された光透過性導電性基板を用意し、平均粒径が１０ｎｍのTiO_2粒子を１１重量％分散したポリエチレングリコールを３０重量％含むアセトニトリル溶液を、浸漬法によりＩＴＯ薄膜上に塗布した。これを８０℃で乾燥したのち、空気中で４００℃で１時間加熱することで、厚さ約１０μｍのTiO_2微粒子膜（３）を形成した。次に、TiO_2微粒子膜を、化５に構造を示したルテニウム金属錯体色素分子を１０ｍＭ溶解したエタノール中に浸漬することで、色素分子をTiO_2微粒子膜に添着した。さらに、これを４－ｔｅｒｔ－ブチルピリジンに浸漬したのち、アセトニトリルで洗浄したのち乾燥することで光触媒電極を作製した。なお、１２は透明のシリコンラバーよりなる封止材である。

【０１０２】

【化５】



【０１０３】電解液・燃料液（５）として０．１ＭＫＯＨ水溶液に炭水化物としてグルコースを５０ｍＭ、ＮＡＤＨを５ｍＭ溶解したものを用いた。電解液・燃料液（５）は、電解液・燃料液注入口（８ａ）より注入され、発電後、排出口（８ｂ）より排出される。空気は、酸素透過性撥水膜（７）を通して外部より発電セル内部に供給される。

【０１０４】発電セルＢは、CoCOOHPcを添着しないMn_2O_3を用いた空気極を使用した以外は、発電セルＡと同じ構成となるように作製した。

【０１０５】光触媒電極は光照射により光活性種（S^+）と電子を生成する。S^+は、ＮＡＤＨ（還元体）より電子を受け取り、元の基底状態種（Ｓ）に戻る。電子を渡したＮＡＤＨは酸化体（NAD^+）となり、このNAD^+は燃料であるグルコース（$C_6H_{12}O_6$）を酸化してグルコースから電子を受け取りＮＡＤＨに戻る。光触媒電極で生成した電子は、外部回路を通り正極である酸素極に至り、酸素（O_2）の還元反応に用いられる。以上の発電反応を以下の反応式で示す。

〈負極〉

$S \rightarrow S^+ + e^-$（外部回路へ）

$NADH + S^+ \rightarrow NAD^+ + S$

$NAD^+ + C_6H_{12}O_6 \rightarrow$

$NADH + C_6H_{11}O_6 + H^+$（正極へ）

〈正極〉

$$1/2O_2 + e^- \text{（外部回路から）} + H^+ \text{（負極から）} \rightarrow 1/2H_2O$$

〈全体反応〉

$$C_6H_{12}O_6 + 1/2O_2 \rightarrow C_6H_{11}O_6 + 1/2H_2O$$

【０１０６】（１４）発電セルの動作特性

上記工程により作製した発電セルを、電解液・燃料液で満たしたのち、ガラス基板（１）側より太陽光シミュレータ（ＡＭ１．５、１００ｍＷ／ｃｍ^2）からの光を照射して、発電セルの起電力（ＯＣＶ）および、１００μＡの一定電流で２０分間放電した際の、発電セルの電圧を測定した。ＯＣＶは、発電セルＡでは、１．３０Ｖ、発電セルＢでは、１．２０Ｖであった。また、２０分間放電後の発電セルの電圧は、発電セルＡでは、１．２０Ｖ、発電セルＢでは、１．０Ｖであった。

【０１０７】本発明の酸素還元複合電極を有する発電セルＡでは、発電セルＢに較べ、高い起電力が得られるとともに、放電に際しても、高い電圧を維持することができた。

【０１０８】（実施例９）

（燃料電池）本発明の酸素還元複合電極を空気極に用い、負極を燃料極とし、空気極と燃料極とをプロトン導電性のイオン交換膜を介して接続して、燃料電池を構成することができる。

【０１０９】図４は、燃料電池の構造の一例を示す模式図である。燃料電池の単セル２０は、空気極２１と燃料極２２とがプロトン導電性の電解質２３を介して接続されている。空気極２１には、空気供給口２４から空気が供給され、反応後、空気排気口２５から排気される。一方、燃料極２２には、燃料供給口２６から水素を含有する燃料ガスが供給され、反応後、燃料排気口２７から排気される。ここで、発電反応を、以下の反応式で示す。

〈負極〉

$$H_2 \rightarrow 2H^+ + 2e^- \text{（外部回路へ）}$$

〈正極〉

$$1/2O_2 + 2H^+ + 2e^- \text{（外部回路から）} \rightarrow H_2O$$

【０１１０】空気極には、例えば、化３に構造式を示したコバルトテトラカルボキシフタロシアニン（CoCOOHPc）を２．０重量％添着したMn_2O_3粉末２重量部、活性炭粉末１重量部、アセチレンブラック粉末０．３重量部、ＰＴＦＥバインダー０．２重量部からなる混合物を混練し、圧延して成るシート状空気極を用いることができる。一方、燃料極には、所定量の白金を担持させたカーボン粒子にＰＴＦＥバインダーを加えて混練し、圧延して成るシート状燃料極を用いることができる。次いで、例えば、ナフィオン１１２等のプロトン導電性イオン交換膜の両面にシート状空気極及びシート状燃料極を圧着して一体化して、単セルを作製する。あるいは、液状のイオン交換膜を空気極及び燃料極の片面に塗布し、乾燥して固化させ、その後、固化したイオン交換膜を介して空気極及び燃料極を圧着して一体化させることもできる。なお、上記の方法で作製した単電池を複数積層して、スタックを構成することもできる。

【０１１１】本発明の酸素還元複合電極を正極に用いることにより、従来に比べ、起電力ならびに放電時の電池電圧が高い燃料電池を得ることができる。

【０１１２】（実施例１０）

（空気電池）本発明の酸素還元複合電極を正極に用い、負極に亜鉛、マグネシウム、アルミニウムなどの金属を用いることにより空気電池を構成することができる。例えば、負極に亜鉛を用いた空気亜鉛電池は、以下の方法により作製することができる。

【０１１３】図５は、空気電池の構造の一例を示す一部切欠断面図である。底部に空気孔３６を有する金属製の正極ケース３７に、底面側から酸素選択透過膜３５、撥水膜３４、空気極３１、セパレータ３３が順次積層されている。一方、金属製の負極ケース３８の中には、亜鉛粉末、ゲル化剤、そしてアルカリ電解液を含有する負極３２が収容され、正極ケース３７と負極ケース３８とはガスケット３９を介して絶縁して封口されている。４０は、空気孔３６を封止する粘着シールである。ここで、撥水膜は、空気極への酸素供給と、電解液の電池外部への漏液を防止する役割を果たす。なお、発電反応を以下の反応式で示す。

〈負極〉

$$Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^- \text{（外部回路へ）}$$

〈正極〉

$$1/2O_2 + H_2O + 2e^- \text{（外部回路から）} \rightarrow 2OH^-$$

【０１１４】正極として作用する空気極に、例えば、化３に構造式を示したコバルトテトラカルボキシフタロシアニン（CoCOOHPc）を２．０重量％添着したMn_2O_3粉末２重量部、活性炭粉末１重量部、アセチレンブラック粉末０．３重量部、ＰＴＦＥバインダー０．２重量部からなる混合物を、厚さ０．２ｍｍのニッケルスクリーンに埋め込み保持させて作製したものを用いることができる。

【０１１５】次に、底部に空気孔を有する金属製の正極ケースに、底面側から酸素選択透過膜、撥水膜、空気

極、セパレータを順次積層する。一方、金属製の負極ケースには、負極活物質として亜鉛粉末、ゲル化剤、そしてアルカリ電解液を含有する負極を収容する。次いで、正極ケースと負極ケースとをガスケットを介して絶縁して密閉する。

【０１１６】本発明の酸素還元複合電極を正極に用いることにより、従来に比べ、起電力ならびに放電時の電池電圧が０．１Ｖから０．５Ｖ程度高い空気電池を得ることができる。

【０１１７】なお、本実施例１０では、負極に亜鉛を用いた例を示したが、亜鉛に代えてマグネシウムあるいはアルミニウムを用いる場合においても、本実施例１０と同様の方法で作製することができ、かつ、同様の効果を有する。

【０１１８】

【発明の効果】本発明によれば、酸素の還元反応を正極反応として用いる亜鉛—空気電池、アルミニウム—空気電池、砂糖—空気電池などの空気電池や、酸素水素燃料電池、メタノール燃料電池などの燃料電池など電気化学デバイスの酸素極あるいは空気極などに用いられる、酸素の電気化学還元に対して、見かけ上、４電子還元反応を１００％に近い選択率で与える安定性にも優れた酸素還元複合電極を提供する。

【図面の簡単な説明】

【図１】　本発明の電極の電流－電圧応答特性を示す図である。

【図２】　本発明の電極の定電位電解時の電流－時間応答を示す図である。

【図３】　本発明の一実施例の発電セルの構造を示す模式断面図である。

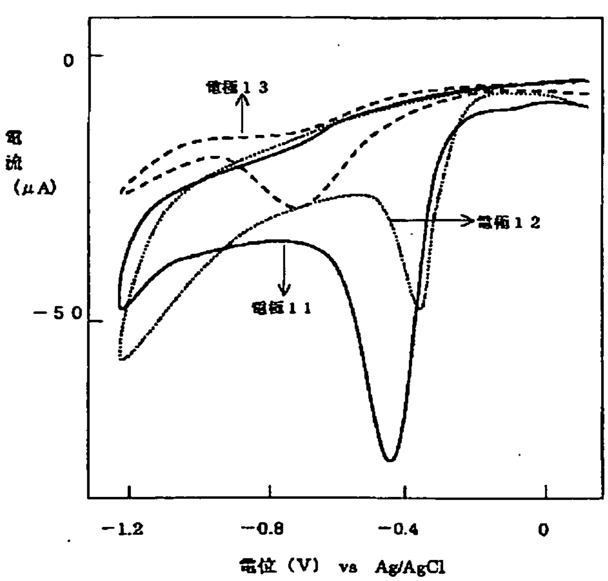
【図４】　本発明の一実施例の燃料電池の構造を示す模式図である。

【図５】　本発明の一実施例の空気電池の構造を示す一部切欠断面図である。

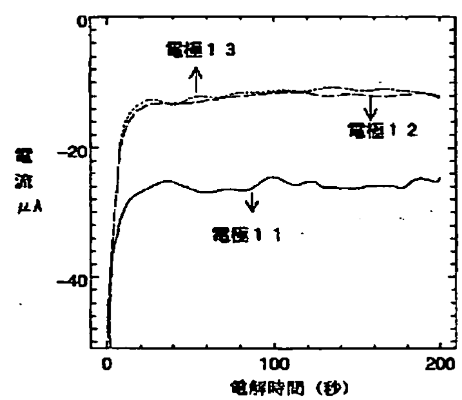
【符号の説明】

１　ガラス基板、２　ＩＴＯ薄膜、３　TiO_2微粒子薄膜、４　色素分子層、５　電解液・燃料液、６　空気極、７　酸素透過性撥水膜、８ａ　電解液・燃料液注入口、８ｂ　電解液・燃料液排出口、９ａ，９ｂ　液バルブ、１０　負極リード、１１　正極リード、１２　封止材、２０　燃料電池の単セル、２１　空気極、２２　燃料極、２３　電解質、２４　空気供給口、２５　空気排気口、２６　燃料供給口、２７　燃料排気口、３０　空気電池、３１　空気極、３２　負極、３３　セパレータ、３４　撥水膜、３５　酸素選択透過膜、３６　空気孔、３７　正極ケース、３８　負極ケース、３９　ガスケット、４０　粘着シート。

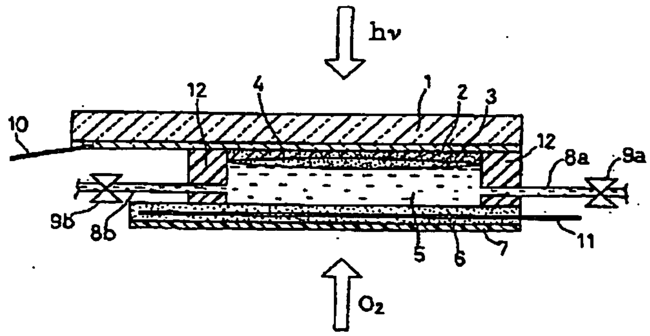
【図１】



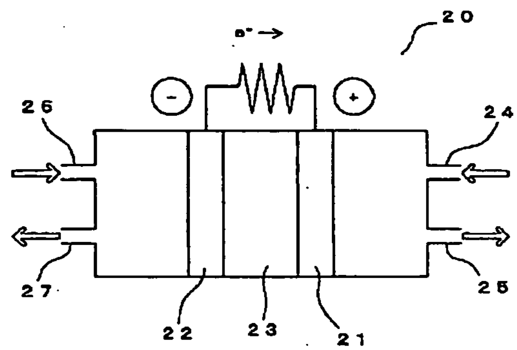
【図２】



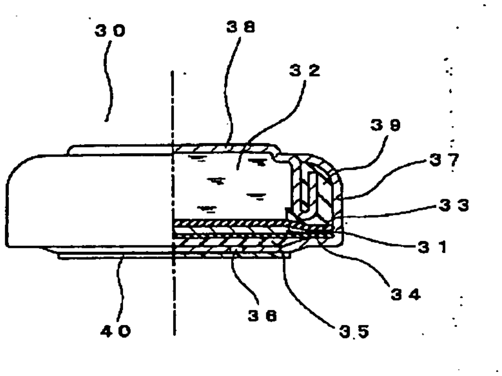
【図３】



【図４】



【図５】



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